

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS ON ORGANIC CHEMISTRY.

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PART I.

Organic Chemistry.

Decomposition of Iodoform by the Action of Oxygen and Light Rays. EDMOND VAN AUBEL (*Chem. Centr.*, 1904, ii, 1376; from *Physikal. Zeit.*, 5, 637. Compare Hardy and Willcock, *Abstr.*, 1903, ii, 622).—Mixtures of iodoform with substances which are not liquid, such as vaselin, are decomposed by sunlight and by radium rays, but when exposed to moderate light in winter at -45° , no decomposition could be detected. E. W. W.

Preparation of Di-iodoacetylene. HEINRICH BILTZ and ERNST KÜPPERS (*Ber.*, 1904, 37, 4412—4416).—The formation of di-iodoacetylene by the interaction of calcium carbide with iodine dissolved in aqueous potassium iodide (Biltz and Werner, *Abstr.*, 1897, i, 389) is due to the calcium hypoiodite, which is produced by the action of calcium hydroxide on iodine, rendering possible a direct substitution by iodine of the hydrogen of acetylene. This is shown by the fact that a good yield of di-iodoacetylene is obtained by passing acetylene gas through ice-cold aqueous potassium hydroxide to which a solution of iodine in aqueous potassium iodide is gradually added. That the hypoiodite itself does not act on the acetylene is proved by the fact that no action takes place on passing the gas through a cold solution of iodine in aqueous sodium hydroxide containing sodium hypoiodite and sodium iodide. W. A. D.

Action of Acetylene on Solutions of Mercuric Chloride. Trichloromercuriacetaldehyde. HEINRICH BILTZ and OTTO MUMM (*Ber.*, 1904, 37, 4417—4427).—The white precipitate which is formed on passing purified acetylene through mercuric chloride solution has not the composition $C_2Cl_2Hg_2$, as assumed by Keiser (*Abstr.*, 1894, i, 61), but is a trichloromercuriacetaldehyde, $C(HgCl)_3 \cdot CHO$; this is shown by analysis, by the fact that in its formation, according to the equation $C_2H_2 + 3HgCl_2 + H_2O = C_2HOCl_3Hg_3 + 3HCl$, three mols. of hydrogen chloride are eliminated, and by its giving acetaldehyde when boiled with hydrochloric acid. The substance supposed by Hofmann (*Abstr.*, 1899, i, 485) to be $C_2Cl_4Hg_3$ is really the same substance. Chlorine water converts trichloromercuriacetaldehyde into mercuric chloride and chloral. The action of iodine is, however, different; using iodine and water or a solution of iodine in aqueous potassium iodide, three atoms of the halogen are absorbed per molecule; with alcoholic iodine, an absorption of 6 atoms is observed. In each case, mercuric iodide was formed, but other products were not isolated. Potassium permanganate in presence of sulphuric acid oxidises trichloromercuriacetaldehyde directly to mercuric salts and carbon dioxide; the formation of trichloromercuriacetic acid (Hofmann, *Abstr.*, 1898, i, 635) was not observed.

The compound formed by the interaction of allylene with mercuric chloride (Kutscheroff, *Abstr.*, 1884, 572 and 719) is *trichloromercuriacetone*, $CH_3 \cdot CO \cdot C(HgCl)_3$; it is decomposed by acids giving acetone. Ethylacetylene and mercuric chloride similarly give *trichloromercurimethyl ethyl ketone*. The salt formed by the action of mercuric acetate on allylene is *mercuriacetone acetate*, $Hg \cdot CAc \cdot Hg \cdot O \cdot CO \cdot CH_3$.

W. A. D.

Action of Acetylene on Mercuric Chloride Solution. KARL A. HOFMANN (*Ber.*, 1904, 37, 4459—4460. Compare *Abstr.*, 1898, i, 635; 1899, i, 97, 485; Biltz and Mumm, preceding abstract).—The compound $C_2Hg_3Cl_4$ is hydrolysed by water so rapidly to the aldehyde, $C(HgCl)_3 \cdot COH$, that a preparation free from oxygen could not be obtained. When warmed with an aqueous solution of potassium cyanide, trichloromercurialdehyde yields aldehyde-resin, mercuric cyanide, and mercury.

No precipitate is formed when acetylene is passed through an aqueous solution of mercuric chloride containing a large excess of sodium chloride.

G. Y.

Formation of Alcohols by Reduction of Acid Amides. II. RUDOLF SCHEUBLE and EMMO LOEBL (*Monatsh.*, 1904, 25, 1081—1105. Compare *Abstr.*, 1904, i, 466).—Reduction with sodium and amyl alcohol of acetamide, heptamide, and azelamide leads to the formation of ethyl alcohol, heptyl alcohol, and nonane- α -diol respectively. *n*-Valeramide, α -methylbutyramide, and $\alpha\alpha$ -dimethylpropionamide are reduced to *n*-amyl alcohol, *sec*-butylcarbinol, and *tert*-butylcarbinol respectively. *n*-Valeramide and $\alpha\alpha$ -dimethylpropionamide have been reduced also by sodium in octyl-alcoholic solution to the corresponding

alcohols. In each case, the formation of the alcohol is accompanied by that of the corresponding amine.

Nonane- α -diol (*enneamethylene glycol*) melts at 45.5° and boils at 177° (corr.) under 15 mm. pressure; the *diacetate*, $C_9H_{18}(OAc)_2$, boils at 161° under 9 mm. pressure; oxidation of the glycol with potassium permanganate in slightly alkaline aqueous solution leads to the formation of azelaic acid. *Nonane- α -diamine* forms a *platinichloride*, $C_9H_2N_2, H_2PtCl_6$. G. Y.

Oxidation of Acetol (Acetylcarbinol). ANDRÉ KLING (*Compt. rend.*, 1904, **139**, 740—742. Compare Abstr., 1900, i, 129; 1901, i, 625; 1903, i, 223; 1904, i, 2, 474; also Nef, following abstract).—When acetol (acetylcarbinol) is oxidised, it yields lactic acid or a mixture of acetic and formic acids according to the nature of the oxidising agent employed. Such oxidising agents as copper hydroxide, ferric hydroxide, mercuric hydroxide, alkaline potassium ferricyanide, and the manganic hydroxides yield chiefly lactic acid with traces of acetic and formic acids, with the probable formation of an acetolate as an intermediate compound; mercuric chloride and copper acetate also yield lactic acid, but the oxidation is much slower and less complete, whilst chromic acid, lead dioxide, nitric acid, barium or sodium peroxide, potassium permanganate, hydrogen peroxide, silver hydroxide, or a mixture of mercuric sulphate and sulphuric acid yield only formic and acetic acids. M. A. W.

Dissociation of the Glycols and of the Glycerols. I and II. JOHN U. NEF (*Annalen*, 1904, **335**, 191—245, 247—333. Compare Abstr., 1901, i, 626; 1902, i, 6).—When passed over pumice stone at 500 — 560° , glycol yields acetaldehyde, crotonaldehyde, carbon monoxide, methane, and hydrogen. Ethylene oxide at 400 — 420° yields acetaldehyde and no gaseous products.

At 500° , propylene oxide forms 2 parts of propaldehyde and 1 part of acetone; under the same conditions, propylene glycol forms propaldehyde only. α -Propaldehydesemicarbazone crystallises in glistening, flat needles and melts at 88 — 90° ; the β -modification crystallises in plates and melts at 154° . The action of hydrogen chloride on propylene oxide at -15° leads to the formation of chloroisopropylalcohol, which, when distilled with phosphoric oxide, yields a mixture of α - and γ -chloropropylenes. When passed over pumice stone at 450° , trimethylene glycol yields acraldehyde, allyl alcohol, *n*-propyl alcohol, and a little propaldehyde; under the same conditions, allyl alcohol yields a small amount of diallyl oxide.

The formation of formaldehyde, acetaldehyde, acraldehyde and their products with unchanged glycerol, when glycerol is passed over pumice stone at 430 — 450° , is explained by the assumption that the glycerol dissociates into $OH \cdot CH_2 \cdot CH < \begin{smallmatrix} CH_2^- \\ O^- \end{smallmatrix}$ and

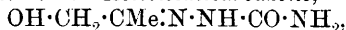


which change into acetol and hydracrylaldehyde respectively. The

acetol further dissociates into formaldehyde and acetaldehyde, the hydracrylaldehyde into water and acraldehyde.

When treated with semicarbazide hydrochloride in aqueous potassium carbonate solution, acraldehyde forms 1-pyrazoline-1-carboxylamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{N} < \begin{array}{c} \text{N} = \text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, which crystallises in glistening

needles and melts at 171° . *Acetolsemicarbazone*,



crystallises in needles and is only sparingly soluble in ether, benzene, chloroform, or water. The *semicarbazone* of hydracrylaldehyde, $\text{C}_4\text{H}_9\text{O}_2\text{N}_3$, forms thick crystals and melts at 114° .

When heated at 250 — 330° , pentaerythritol yields a distillate which, with semicarbazide hydrochloride in potassium carbonate solution forms a semicarbazone. This melts at 183° , and when recrystallised from water forms 5-methylpyrazoline-1-carboxylamide, which crystallises in glistening needles and melts at 198° . As acraldehyde is converted into crotonaldehyde in alkaline solution, the reaction for crotonaldehyde with semicarbazide must be carried out in slightly acid solution.

Glycerol ether (Zotta, *Annalen*, 1874, 174, 87) is identical with

β -acraldehydeglycerol, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \\ | \\ \text{CH} < \begin{array}{c} \text{O} - \text{CH} \\ | \quad | \\ \text{O} - \text{CH}_2 \end{array} \end{array}$; its formation along with

the β -modification, and small amounts of acetol and acetaldehydeglycerol, from glycerol when heated with ammonium chloride at 270 — 330° , is ascribed to conversion of part of the glycerol into α - and β -chlorohydrins, which dissociate, forming acetol and hydracrylaldehyde.

The formation of allyl alcohol when glycerol is heated with oxalic acid is explained by the formation and dissociation of diformin and reduction of the propargyl alcohol formed by the formic acid. When heated with oxalic acid, glycol yields the monoformate and carbon dioxide; trimethylene glycol and oxalic acid form the monoformate of trimethylene glycol and carbon dioxide.

Glycide is obtained by the action of alcoholic potassium hydroxide on α -chlorohydrin; when heated for 5 hours in a sealed tube at 200 — 220° , it forms a yellow resin, which is easily soluble in water and, when heated, decomposes with evolution of formaldehyde; glycide does not reduce Fehling's solution; when heated with water at 100° , it yields glycerol; with absolute alcohol, it forms the α -ethyl ether of glycerol. α -Nitroglycerol is formed by the action of water on glycide nitrate, but only to a very small extent by the action of dilute nitric acid on glycide (compare Hanriot, *Ann. Chim. Phys.*, 1879, [v], 17, 118). At 450° , glycide dissociates into carbon monoxide, hydrogen, methane, acetaldehyde, acetol, and traces of acraldehyde.

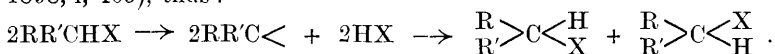
The reactions of epichlorohydrin are explained by assuming that it dissociates into the "active molecule," $\text{CH}_2\text{Cl} \cdot \text{CH} < \begin{array}{c} \text{CH}_2^- \\ | \\ \text{O} \end{array}$. Epi-iodohydrin is formed by the action of potassium iodide on epichlorohydrin in alcoholic solution and treatment of the α -di-iodohydrin so formed with aqueous sodium hydroxide; it boils at 62° under 24 mm.

pressure. *Glycide nitrate*, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}_2$, formed by the action of silver nitrate on epi-iodohydrin in ethereal solution, boils at 62—64° under 15 mm. pressure, has a sp. gr. 1.324 at 21.3°, decomposes above 200°, and yields α -nitroglycerin when heated with water.

Diglycide ether, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$, formed when epi-iodohydrin is heated with silver oxide and ether at 60—100°, is a colourless oil, boils at 103° under 22 mm. pressure, has a sp. gr. 1.119 at 23°, and when heated with water at 100°, forms *bisdihydroxypropyl oxide*, $[\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2]_2\text{O}$, which boils at 261—262° under 27 mm. pressure. Diglycide ether dissociates at 440—450° with formation of metaformaldehyde, acetaldehyde, and crotonaldehyde.

When passed over pumice stone heated to 450°, glycide ethyl ether yields acetaldehyde, acetol ethyl ether, and an oil which boils at 80—85° under 23 mm. pressure and is perhaps the diethyl ether, $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{OEt})_2$. The semicarbazone of acetol ethyl ether, $\text{C}_6\text{H}_{13}\text{O}_2\text{N}_3$, forms a white, crystalline powder and melts at 92°.

The formation of pyruvic acid from glyceric and from tartaric acid, and of phenylacetaldehyde and carbon dioxide from phenylglyceric acid, and the behaviour of $\alpha\beta$ -glycols (chlorohydrins, &c.) with zinc chloride and potassium hydrogen sulphate are explained on the assumption of an "ethylidene dissociation"; the second stage, that of isomerisation, may be replaced by addition of the dissociated parts so as to form a mixture of optically active isomerides (Walden, Abstr., 1898, i, 405), thus :



The action of dilute acids on $\alpha\beta$ -glycols is discussed (compare Krassuski, Abstr., 1902, i, 425; Lieben, Abstr., 1902, i, 336).

Acetylcarbinol is best prepared by boiling chloro- or bromo-acetone with anhydrous potassium or sodium formate in methyl-alcoholic solution in a reflux apparatus. It is formed also by hydrolysis of acetylcarbinyl acetate with methyl alcohol at 140°, by hydrolysis of the acetate or formate of r -lactic aldehyde with methyl alcohol or water at 180°, and from r - α -bromopropaldehyde by the action of potassium formate in boiling methyl-alcoholic solution or by the action of potassium acetate in alcoholic solution at 100°. The polymerisation of acetylcarbinol is prevented by dilution with an equal volume of methyl-alcohol, provided that no trace of acetic or formic acid is present. Acetylcarbinolphenylhydrazone is formed by the action of phenylhydrazine on acetol in presence of sodium hydroxide in aqueous methyl-alcoholic solution; it melts at 106° (m. p. 100—102°; Pinkus, Abstr., 1898, i, 224). The action of sodium hydroxide and phenylhydrazine on dextrose in aqueous methyl-alcoholic solution leads to the formation of acetolosazone, but no acetylcarbinolphenylhydrazone, therefore pyruvic aldehyde, and not acetol, is the intermediate product in the formation of r -lactic acid from dextrose by the action of sodium hydroxide. The formation of acetylcarbinol on addition of sodium hydroxide to fused dextrose is due to reduction of the pyruvic aldehyde first formed

by atomic hydrogen. Acetylcarbinolosazone which melts at 150—154° (compare Perkin, Trans., 1891, **59**, 796), is formed by the action of phenylhydrazine on acetylcarbinol, *r*-lactic aldehyde, or pyruvic aldehyde in 50 per cent. acetic acid.

Bisacetylcarbinol dimethyl ether, $\text{OMe} \cdot \text{CMe} < \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{O} \end{smallmatrix} > \text{CMe} \cdot \text{OMe}$, formed by the action of formic or acetic acid or methyl-alcoholic hydrochloric acid on acetylcarbinol in methyl-alcoholic solution, melts at 127° and boils at 193—194° (m. p. 130°; b. p. 196°; Henry, *Bull. Soc. chim.*, 1883, **39**, 526); it crystallises in monoclinic plates [$a:b:c=1.77246:1:2.00865$; $\beta=84^\circ 13'$] and yields acetylcarbinol and methyl alcohol when boiled with dilute hydrochloric acid. Hydroxyacetoxime (Piloty and Ruff, Abstr., 1897, i, 587) boils at 123—125° under 18 mm. pressure. Acetylcarbiny acetate, formed by the action of glacial acetic acid and sodium acetate on bromoacetone, is an oil with a sweet odour, boils at 73—74° under 18 mm. pressure, and forms an *oxime*, which boils at 118—119° under 16 mm. pressure, and a *semicarbazone*, $\text{C}_6\text{H}_{11}\text{O}_3\text{N}_3$, which crystallises in thick, flat needles and melts at 145°. When passed through a tube heated to 430—450°, acetylcarbiny acetate yields a somewhat volatile oil consisting principally of acetaldehyde with a small amount of crotonaldehyde and acetic acid.

β -Bromopropaldehydeacetal, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$, formed by the action of hydrogen bromide on acraldehyde in alcoholic solution, boils with slight decomposition at 80—90° under 20 mm. pressure, and when warmed with water yields ethyl alcohol and β -bromopropaldehyde hydrate, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH})_2$, which boils at 40—45° under 18 mm. pressure and has sp. gr. 1.36 at 22°. α -Bromopropaldehyde, formed by the action of bromine on propaldehyde in acetic acid solution, boils at 42—44° under 63 mm. pressure, has a sp. gr. 1.523 at 21°, and dissolves in water or alcohol with development of heat. α -Iodopropaldehyde, obtained by treating α -bromopropaldehyde with a cold saturated solution of potassium iodide, boils at 40° under 15 mm. pressure, and, when heated with silver acetate and ether at 100°, yields the *acetate* of *r*-lactaldehyde, which is an oil of aromatic odour, boils at 55—65° under 19 mm. or at 52—55° under 15 mm. pressure, develops heat when treated with water or alcohol, and is hydrolysed by water at 100° to acetic acid and acetylcarbinol. The *semicarbazone*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \cdot \text{CHMe} \cdot \text{OH}$, crystallises in flat, glistening needles and melts at 163°.

When heated with acetic anhydride in a sealed tube at 100°, acetylcarbinol yields acetylcarbiny acetate; benzoylcarbinol and acetic anhydride at 100° form ω -acetoxycetophenone, which is also formed by the action of ω -bromoacetophenone on silver acetate and is isomeric with mandelaldehyde acetate, obtained from α -bromophenylacetaldehyde, and silver acetate. Acetol and benzoylcarbinol, therefore, are hydroxyketones and are isomeric with lactaldehyde and hydroxyphenylacetaldehyde respectively (compare Kling, Abstr., 1903, i, 138, 223).

Acetylcarbinol reduces cupric hydroxide in aqueous sodium hydroxide solution to cuprous oxide at the ordinary temperature; the resulting

solution contains *r*-lactic acid, but not more than traces of acetic or formic acid. Copper acetate is reduced to cuprous oxide, or copper sulphate to metallic copper, by acetylcarbinol or benzoylcarbinol in aqueous solution; the former yields *r*-lactic acid, the benzoylcarbinol yields, at the ordinary temperature, benzoylformaldehyde, which, when treated with aqueous sodium hydroxide, or when heated with aqueous copper acetate or sulphate solution, is converted into *r*-mandelic acid. A mixture of acetaldehyde and formaldehyde does not reduce cupric hydroxide or copper salts under the same conditions as does acetylcarbinol, the reducing power of which is explained on the assumption of "ethylidene dissociation": $\text{Ac}\cdot\text{CH}_2\cdot\text{OH} = \text{Ac}\cdot\text{CH}\cdot + \text{H}_2\text{O}$, $\text{Ac}\cdot\text{CH}\cdot + 2\text{H}_2\text{O} = \text{Ac}\cdot\text{CH}(\text{OH})_2 + 2\text{H}\cdot$; the reduction is caused by the liberated hydrogen, and the acetyl formaldehyde hydrate undergoes isomeric change into *r*-lactic acid. In aqueous or acid solution, acetol dissociates to acetaldehyde and formaldehyde, so that on oxidation with silver oxide, mercuric oxide, or potassium dichromate and sulphuric acid it yields acetic and formic acids and carbon dioxide. Acetylcarbinol, acetylcarbinyl acetate, and chloro- or bromo-acetone react with solid alkali hydroxides with development of heat and formation of a red resin, $(\text{Ac}\cdot\text{CH})_x$?, which is also formed by the action of 20 per cent. aqueous potassium or sodium hydroxide, or slowly by the action of aqueous sodium carbonate on acetol.

Decompositions of glycerol, sodium glyceroxide, glyceric, lactic, and pyruvic acids, the action of alkali hydroxides on the glycols, and the oxidation of the glycols and of glycerol are discussed from the point of view of the author's dissociation hypothesis.

As glycerol, when heated with 1 mol. of sodium hydroxide, yields propylene glycol, and, when treated with sodium hydroxide and mercuric oxide, forms *r*-glyceric acid, sodium glyceroxide must have the constitution $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{ONa}$. Contrary to statements in the literature, glycerol, when heated with an excess of potash-lime at 260° , yields chiefly carbon dioxide and propionic acid. With *p*-nitrobenzoyl chloride, sodium glyceroxide yields *glyceryl tri-p-nitrobenzoate*, which crystallises in colourless needles and melts at 192° , and *di-p-nitrobenzoate*, which forms colourless plates and melts at 137° .

When heated with $1\frac{1}{2}$ parts of 15 per cent. aqueous sodium hydroxide in a sealed tube at 40 — 50° , *r*-glyceraldehyde, dextrose, and lævulose yield the same amounts of *r*-lactic and trihydroxy-*n*-butyric acids. When warmed with dilute sodium hydroxide and cupric hydroxide, *r*-glyceraldehyde yields *r*-glyceric acid, whilst dextrose and lævulose form chiefly trihydroxy-*n*-butyric acid and no glyceric acid. G. Y.

Action of Hydrogen Bromide or Hydrogen Chloride on Triacetin. **New Halogen Derivatives of Triacetin.** R. DE LA ACEÑA (*Compt. rend.*, 1904, 139, 867—868).—*aa-Dibromomonoacetin* ($\alpha\gamma$ -*dibromo-β-acetylgllycerol*), $\text{OAc}\cdot\text{CH}(\text{CH}_2\text{Br})_2$, obtained by the prolonged action of hydrogen bromide on triacetin, or by heating the mixture at 100° in sealed tubes, boils at 130 — 135° under 40 mm. pressure, has a sp. gr. 1.5880 at 15° , has an agreeable aromatic odour, is slightly soluble in water, and readily so in alcohol or ether, and yields isopropyl alcohol on reduction. *a-Bromodiacetin* (α -*bromo-βγ*-

diacetylgllycerol), $\text{CH}_2\text{Br}\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$, produced by the prolonged action of an acetic acid solution of hydrogen bromide on an ethereal solution of triacetin at 0° in the dark, boils at $150\text{--}155^\circ$ under 40 mm. pressure, has a sp. gr. 1.2905 at 15° , and yields isopropylene glycol on reduction. *aa-Dichloromonoacetin* (*ay-dichloro- β -acetylgllycerol*), prepared similarly to the bromine compound, boils at $115\text{--}120^\circ$ under 40 mm. pressure and has a sp. gr. 1.1618 at 15° . *a-Chlorodiacetin* (*a-chloro- $\beta\gamma$ -diacetylgllycerol*) boils at $145\text{--}150^\circ$ under 40 mm. pressure and has a sp. gr. 1.1307 at 15° . *a β -Dichloromonoacetin*, prepared by the action of acetic anhydride on chlorinated allyl alcohol, has a sp. gr. 1.1677 at 15° , but in all other respects is identical with the *aa*-isomeride. *a-Iododiacetin*, obtained by the action of sodium iodide on the corresponding chlorine compound, is an unstable oil having a sp. gr. 1.4584 at 15° .

M. A. W.

Resemblance between Iron Salts of Organic Acids and Salts of Nitro-derivatives. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1062—1067).—All the monobasic organic acids give ferric salts which dissolve in ether with formation of a red coloration similar to that given by primary and secondary nitro-derivatives. The sensitiveness of the reaction is less with the organic acids than with the nitro compounds; in applying the test to the latter substances, it is necessary to get rid of any free acid by means of soda. The ferric salts of the organic acids are formed to a slight extent by the action of ferric chloride, hydroxide, or basic carbonate on the free acid in aqueous solution. They are formed more readily by the interaction of the free organic acid and iron reduced by hydrogen, and still more readily by the action of ferric chloride on the free acid in aqueous alcoholic solution.

T. H. P.

[**Electrolysis of Potassium Acetate.**] HANS HOFER and M. MOEST (*Zeit. Elektrochem.*, 1904, 10, 833—834).—Foerster and Piguet (*Abstr.*, 1904, i, 965) appear to have overlooked the authors' paper (*Abstr.*, 1902, i, 736), in which it was shown that methyl alcohol is always formed in the electrolysis of potassium acetate. This formation of methyl alcohol accounts for the deficit of ethane observed, and also for the formation of carbon dioxide, without assuming the anodic oxidation of acetic acid, a reaction which it has been proved does not take place to any appreciable extent in acid solutions.

T. E.

Composition of Homologues of "Schweinfurt's Green." GEORGES VIARD (*Bull. Soc. chim.*, 1904, iii, 31, 1138—1142).—A series of homologues of this pigment have been prepared using formic, propionic, and *n*- and isobutyric acids in place of acetic acid. They closely resemble Schweinfurt's green in appearance and properties (the formic acid derivative decomposes above 170° and the others above 200° , evolving arsenious oxide), and have compositions corresponding with the typical formula $\text{CuAc}_2\cdot 3\text{Cu}(\text{AsO}_2)_2$ (compare Wöhler and Springmann, *Annalen*, 1855, 94, 44, and Abraham, *Chem. News*, 1870, 21, 265). These products are best obtained when precipitation is carried out in presence of a small quantity of the respective organic acid. When there is no free acid present, the true Schweinfurt's green is only formed in the later stages, and the first products are

yellowish-green substances, richer in copper and poorer in arsenic than the true pigments. The latter, even when produced at the ordinary temperature do not contain water of crystallisation. T. A. H.

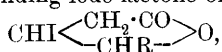
β -Bromobutyric Acid. ROBERT LESPIEAU (*Compt. rend.*, 1904, 139, 738—739).— β -Bromobutyramide, $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared by the action of hydrobromic acid on allyl cyanide in the cold, crystallises from boiling chloroform in white crystals melting at $92-93^\circ$, and is converted into crotonamide, $\text{CHMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$, by the action of normal potassium hydroxide solution. β -Bromobutyric acid, $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$,

prepared by hydrolysing the corresponding amide by means of warm hydrobromic acid, melts at $17-18^\circ$ and boils at 122° under 16 mm. pressure; the *ethyl* ester, prepared by saturating an alcoholic solution of the acid with hydrobromic acid, boils at 183° under 755 mm. pressure; α -bromobutyric acid melts at -4° and boils at $114-115^\circ$ under 20 mm. pressure. β -Bromobutyric acid loses HBr by the action of potassium hydroxide, and is converted into crotonic acid. These facts afford direct evidence in favour of Pinner's explanation of the formation of crotonic acid from allyl cyanide (compare Abstr., 1880, 99). M. A. W.

Synthesis of Nitro-esters. CELSO ULPANI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 346—349).—In the method previously described by the author (Abstr., 1903, i, 791) for the synthesis of nitro-esters from ethyl nitromalonate, the yield obtained diminishes as the molecular weight of the alkyl iodide employed increases. Even in the case of ethyl α -nitrobutyrate, it is best not to use this method of synthesis, but to nitrate ethyl ethylmalonate directly and then to decarboxylate by means of sodium ethoxide. The latter method is generally applicable where the conditions of complete nitration of the ethyl alkylmalonate are known. Ethyl ethylmalonate, for example, is completely nitrated by standing for 48 hours in contact with fuming nitric acid, yielding ethyl nitromalonate, which, when treated with sodium ethoxide and the solution acidified, gives *ethyl α -nitrobutyrate*, $\text{CHEt}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$, as an oil boiling at about 123° under 20 mm. pressure. The *sodium* derivative is readily soluble in water, alcohol, ethyl acetate, and acetone, and the *ammonium* compound crystallises in nacreous laminae, which in a desiccator lose ammonia and liquefy.

T. H. P.

Action of Iodine and Yellow Oxide of Mercury on Acids containing an Ethylenic Linking. Separation of Isomerides. J. BOUGAULT (*Compt. rend.*, 1904, 139, 864—867. Compare Abstr., 1900, i, 495, 641; 1901, i, 383).—Unsaturated acids of the type $\text{CHR}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, containing the ethylenic linking in the $\alpha\beta$ -position, and of the type $\text{CH}_2\cdot\text{CR}\cdot\text{CO}_2\text{H}$, do not react with iodine and yellow mercuric oxide (nascent hypoiodous acid); the acids containing the ethylenic linking in the $\beta\gamma$ position react readily with hypoiodous acid to form the corresponding iodo-lactone of the type



which is insoluble in alkalis, generally crystalline, and the yield is quantitative. Hypoiodous acid is, therefore, a convenient reagent for separating $\beta\gamma$ -unsaturated acids from their $\alpha\beta$ -isomerides, and 0.01 gram of hydropiperic ($\beta\gamma$) or hydrosorbic ($\beta\gamma$) acid was thus separated from 3 or 4 grams of the $\alpha\beta$ -isomeride. Unsaturated acids of the type $\text{CHR}:\text{CH}\cdot[\text{CH}_2]_n\text{CO}_2\text{H}$ ($n > 2$) react readily with hypoiodous acid to form saturated compounds having the formula $\text{OH}\cdot\text{CHR}\cdot\text{CHI}\cdot[\text{CH}_2]_n\text{CO}_2\text{H}$ or $\text{CHRI}\cdot\text{CH}(\text{OH})\cdot[\text{CH}_2]_n\text{CO}_2\text{H}$.

M. A. W.

Drying Process of Linseed Oil. WILHELM FAHRION (*Chem. Zeit.* 1904, 28, 1196—1200. Compare Abstr., 1904, ii, 217).—An historical survey of work done on the chemical changes involved during the drying of linseed oil. The subject is discussed from the point of view of Engler's auto-oxidation theory.

A. McK.

Elæomargaric Acid. MORITZ KITZ (*Chem. Rev. Fett. Ind.*, 1904, 11, 190).—Elæomargaric acid, obtained from the fruit of *Aleurites cordata*, changes after a few hours' exposure to air, being gradually oxidised to a resin. When oxidised by alkaline permanganate, it forms traces of dihydroxystearic acid, whilst a solid fatty acid, melting between 97° and 102° , together with considerable amounts of volatile fatty acids, is also produced.

A. McK.

Preparation of α -Ketonic Acids and Esters from α -Oximino-esters. (Part V.) LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, iii, 31, 1142—1147. Compare Abstr., 1904, i, 849).—The α -oximino-esters of the type $\text{NOH}\cdot\text{CR}\cdot\text{CO}_2\text{Et}$ (*loc. cit.*) are partially hydrolysed into the corresponding ketonic esters by heating in sealed tubes with hydrogen chloride dissolved in alcohol, but the separation of the products from this liquid is difficult. The results of a number of experiments with oxidising agents having for their object the elimination of the oximino-group show that products capable of yielding nitrous acid are most suitable for the purpose. The following method is recommended. The oximino-ester is dissolved in twice its weight of formic acid containing 15 per cent. of water and ether sufficient to form a layer added. The whole is cooled to 0° , and the requisite quantity of nitrosylsulphuric acid added gradually, so that the temperature does not rise beyond 25 — 30° . The liquid is cooled and poured into five times its weight of ice, and the ethereal layer separated, washed with a little water, dried, and the ether distilled off. The residue, after the removal of formic acid by fractional distillation, contains some unchanged α -oximino-ester, in addition to the required α -ketonic ester and any free acid produced by the hydrolysis of the latter (the butyl- and amyl-esters are most resistant to hydrolysis). The free acid is removed by agitation with a dilute solution of sodium carbonate, and the unchanged oximino-ester by fractional distillation.

From the α -ketonic esters so prepared, the acids are obtained by heating with water in sealed tubes at 150 — 160° (compare Bouveault and Wahl, Abstr., 1901, i, 252), but in the case of the hexyl and higher esters saponification with alkaline solutions may be resorted to.

T. A. H.

α -Ketonic Acids and Esters (Homopyruvic Compounds). RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1147—1153. Compare Abstr., 1904, i, 849 and preceding abstract).—These esters are colourless or slightly yellow liquids, readily saponified by alkalis, and in the case of the first members of the series by water alone. The acids distil under reduced pressure. The melting points recorded below were determined on the mercury-bath. The following products have usually been prepared by the methods described in the preceding abstract.

Ethyl α -ketobutyrate, $\text{COEt} \cdot \text{CO}_2\text{Et}$ (compare Aristoff and Demjanoff, Abstr., 1888, 251), obtained in minute quantity by the prolonged action of hydrochloric acid on a mixture of ethyl ethylbutyrylacetate and sodium nitrite dissolved in water, is very soluble in water, boils at 75° under 20 mm. pressure, and at 162° under 760 mm. pressure.

Ethyl α -ketovalerate is obtained to the extent of 10—15 per cent. by the general method, the remainder being hydrolysed; it boils at 72 — 77° under 10 mm. pressure and furnishes a crystalline *semicarbazone* which melts at 139 — 140° (corr.). The corresponding acid was characterised by its phenylhydrazone (compare Brunner, Abstr., 1895, i, 335).

isoButyl α -ketovalerate, of which a yield of 30 per cent. was obtained, boils at 87 — 88° under 11 mm. pressure, has sp. gr. 0.973 at $0^\circ/4^\circ$; the *semicarbazone* separates from benzene and light petroleum in spangles, becomes anhydrous at 90° , and melts at 137 — 138° (corr.). Ethyl α -ketoisohexoate boils at 74° under 11 mm. pressure and at 93° under 25 mm. pressure, the *semicarbazone* crystallises in spangles and melts at 158 — 159° (corr.). The corresponding acid, prepared by the general method (Bouveault and Wahl, Abstr., 1901, i, 252), boils at 84 — 85° under 15 mm. pressure and melts at -1.5° ; the *semicarbazone*, which is a slightly soluble powder, melts at 205° (corr.). Ethyl α -ketoisooheptoate, a liquid of agreeable odour, boils at 93 — 94° under 12 mm. pressure, and has sp. gr. 0.979 at $0^\circ/4^\circ$; the *semicarbazone* crystallises from a mixture of alcohol and benzene in spangles and melts at 162 — 163° (corr.); the corresponding acid (compare Fittig and Kaehlbrandt, Abstr., 1899, i, 418) was obtained by hydrolysing the ester with a dilute solution of potassium hydroxide; the *semicarbazone* crystallises from dilute alcohol and melts and decomposes at 205.5° (corr.).

Ethyl α -keto- β -methylmonoate, $\text{C}_6\text{H}_{13} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{CO}_2\text{Et}$, a mobile liquid, boils at 123 — 124° under 12 mm. pressure, and has a sp. gr. 0.944 at $0^\circ/4^\circ$; the *semicarbazone* is amorphous; the corresponding acid is a slightly viscous oil boiling at 124 — 125° under 9 mm. pressure, has sp. gr. 0.991 at $0^\circ/4^\circ$, and yields a *semicarbazone* which crystallises from benzene and melts at 121 — 121.5° (corr.).

T. A. H.

Hydrogenation of Esters of Unsaturated Acids. LOUIS BOUEVAULT and GUSTAVE BLANC (*Bull. Soc. chim.*, 1904, [iii], 31, 1206—1210. Compare Abstr., 1903, i, 597, 673; 1904, i, 642).—The esters of unsaturated acids are readily reduced to the corresponding unsaturated primary alcohols by sodium and absolute alcohol,

except in cases where the ethylenic linking occupies the $\alpha\beta$ -position with reference to the carboxyl group. In the latter case, the corresponding saturated primary alcohols are produced, thus affording, in conjunction with Reformatsky's method of condensing aldehydes and ketones with α -halogenated acids to form $\alpha\beta$ -unsaturated acids, a convenient method of preparing complex alcohols of the type $\text{CH}_2\text{R}\cdot\text{CHR}'\cdot\text{CH}_2\cdot\text{OH}$ and $\text{CHRR}'\cdot\text{CHR}''\cdot\text{CH}_2\cdot\text{OH}$.

Ethyl β -hydroxy- β -methylnonoate, $\text{C}_6\text{H}_{13}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, prepared by condensing methyl hexyl ketone with ethyl iodoacetate in presence of zinc or magnesium, is a colourless, slightly viscous liquid, which boils and decomposes at 138° under 17 mm. pressure; when dissolved in acetic acid and boiled with zinc chloride, it yields *ethyl β -methyl- Δ^{α} -nonenoate*, $\text{C}_6\text{H}_{13}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$; this is a colourless liquid, which boils at 119 – 120° under 14 mm. pressure and has a sp. gr. 0.907 at $0^\circ/4^\circ$, and on reduction furnishes γ -methylnonyl alcohol, $\text{C}_6\text{H}_{13}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, which is a mobile liquid boiling at 111 – 116° under 14 mm. pressure and having a sp. gr. 0.856 at $0^\circ/4^\circ$.

The same cycle of operations applied to methylheptanone gives rise in turn to *ethyl β -hydroxy- $\beta\zeta$ -dimethyloctoate* and *ethyl $\beta\zeta$ -dimethyl- Δ^{α} -octenoate* (β -isohexylcrotonate), the latter on reduction gives $\gamma\eta$ -dimethyloctyl alcohol (dihydro-rhodinol, or citronellol, or tetrahydro-geraniol), a colourless liquid of pleasant odour, boiling at 118° under 15 mm. pressure and having a sp. gr. 0.849 at $0^\circ/4^\circ$; the *pyruvate* boils at 140 – 145° under 13 mm. pressure (compare Bouveault, Abstr., 1904, i, 465). Cinnamic acid on reduction gives rise to γ -phenyl-propyl alcohol, which boils at 235° . Ethyl oleate, on reduction, gives *oleyl alcohol* mixed with elaidyl alcohol?; this is a colourless, viscous liquid, which boils at 200° under 13 mm. pressure and has a sp. gr. 0.862 at $0^\circ/4^\circ$, and furnishes a *phenylurethane*, apparently not homogeneous, which melts at 38° . Undecenoic acid gives the corresponding *alcohol*; this is a colourless, mobile liquid, which boils at 132 – 133° under 15 mm. pressure and has a sp. gr. 0.860 at $0^\circ/4^\circ$; the *phenylurethane* crystallises well and melts at 55° . T. A. H.

Hydrogenation of Esters of Acids with an Acetal Function.

LOUIS BOUVEAULT and GUSTAVE BLANC (*Bull. Soc. chim.*, 1904, [iii], 31, 1210–1213).—The esters of hydroxy- and amino-acids are not reduced by sodium and alcohol. For the preparation of glycols, the authors have therefore had recourse to the reduction of esters of alkyloxy-acids of the type $\text{OR}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$. The position of the OR-group with reference to the carboxyl group exerts a considerable influence on the course of this reaction. When it is in the α -position, it is replaced by an atom of hydrogen forming a simple alcohol, whereas when it occupies the β -position normal reduction takes place with the formation of a monoalkyl glycol. Ethyl β -ethoxypropionate furnishes the *monoethylin* of *trimethyleneglycol*, $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$; this is a colourless liquid, which is soluble in water, boils at 160° , and has a sp. gr. 0.936 at $0^\circ/4^\circ$; the *pyruvate-semicarbazone* is crystalline and melts at 127 – 128° .

Ethyl β -ethoxycrotonate, $\text{OEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, furnishes on reduction

butyric acid and a neutral compound, $\text{OEt} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, which boils at 168° .

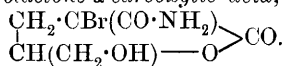
Propyl $\gamma\gamma$ -diethoxyvalerate, $\text{CMe}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Pr}^3$, prepared by condensing propyl lævulate with ethyl iminoformate hydrochloride in presence of alcohol, is a colourless liquid, boils at 115 – 120° under 15 mm. pressure, and on reduction yields a small quantity of a neutral product ($\text{C}_9\text{H}_{20}\text{O}_3$?) which boils indefinitely between 140° and 170° .
T. A. H.

Reduction of Esters of Hydroxy- and Ketonic Acids. LOUIS BOUVEAULT and GUSTAVE BLANC (*Bull. Soc. chim.*, 1904, [iii], 31, 1213–1216. Compare preceding abstract).—Ethyl β -hydroxy- β -methylnonoate on reduction with sodium and absolute alcohol furnishes Bouis's octyl alcohol (β -octanol) and the pinacone corresponding with methyl hexyl ketone. Ethyl β -hydroxydihydrogeranate (Barbier and Bouveault, *Abstr.*, 1896, i, 445) behaves similarly, yielding methylheptenol and the corresponding pinacone; ethyl β -hydroxy- β -phenylpropionate furnishes coumaric acid.

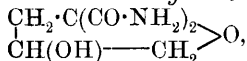
The esters of pyruvic and lævulic acids when reduced in this way do not yield well defined products, but better results are obtained with the β -ketonic esters; thus ethyl α -isobutylacetoacetate yields isohexyl alcohol and isohexoxic acid; ethyl α -allylacetoacetate furnishes Δ^6 -pentenyl alcohol, which boils at 139 – 142° and has a sp. gr. 0.863 at $0^\circ/4^\circ$, and ethyl methylpropylacetoacetate gives β -methylamyl alcohol, which boils at 146 – 148° and has an odour like that of amyl alcohol.

T. A. H.

$\gamma\delta$ -Dihydroxypropylmalonic Acid. WILHELM TRAUBE (*Ber.*, 1904, 37, 4540–4544).—Bromine reacts with an acetic acid solution of Traube and Lehmann's dihydroxypropylmalonamide (*Abstr.*, 1899, i, 417; 1901, i, 501) yielding ammonium bromide and the amide of α -bromo- δ -hydroxyvalerolactone- α -carboxylic acid,



This latter is readily soluble in all solvents, but may be crystallised from ethyl acetate in the form of colourless prisms melting at 109° . It readily reacts with concentrated ammonia yielding the amide of 3-hydroxytetrahydrofuran-1:1-dicarboxylic acid,



which yields the free acid on hydrolysis with sodium hydroxide. This acid is most readily purified by means of its lead salt, which is only sparingly soluble in water; the acid crystallises from water in large cubes containing $1\text{H}_2\text{O}$, which it loses at 130° . When the aqueous solution is heated at 150 – 160° , carbon dioxide is evolved and 3-hydroxytetrahydrofuran-1-carboxylic acid is obtained. This crystallises in well developed prisms and melts at 110° .
J. J. S.

Anhydrides of Saturated Dibasic Acids and Baeyer's Tension Theory. GERARDUS L. VOERMAN (*Rec. Trav. Chim.*, 1904, 23, 265–282).—The conclusions arrived at have already been given

(Abstr., 1904, i, 287). The present paper contains details of the experimental work. T. A. H.

Action of Pyridine and Quinoline Bases on Bromosuccinic and Dibromosuccinic Esters. LOUIS DUBREUIL (*Compt. rend.*, 1904, 139, 870—871. Compare Abstr., 1904, i, 189).—Ethyl bromosuccinate is converted quantitatively into methyl fumarate boiling at 215—220° and melting at -2° by the direct action of excess of pyridine, quinoline, or quinaldine, the hydrogen bromide uniting with the excess of the base to form pyridine hydrobromide, C_5H_5NHBr , melting at 191°, *basic quinoline hydrobromide*, $(C_9H_7N)_2 \cdot HBr \cdot 2H_2O$, melting at 41°, and *basic quinaldine hydrobromide*, melting at 54°, respectively; all these salts are deliquescent, and the two last are decomposed by water. Ethyl dibromosuccinate is converted into ethyl bromomaleate by the action of quinoline or quinaldine, the basic hydrobromides of the bases being formed at the same time, and into ethyl acetylenedicarboxylate by the action of pyridine. M. A. W.

Solubility of the Tartrates of the Alkaline Earths in Water. H. CANTONI and Mile. ZACHODER (*Bull. Soc. chim.*, 1904, [iii], 31, 1121—1124).—The solubilities of calcium tartrate, $CaC_4H_4O_6 \cdot 4H_2O$, strontium tartrate, $SrC_4H_4O_6 \cdot 3H_2O$, and barium tartrate, $BaC_4H_4O_6$, have been determined at various temperatures between 0° and 60°. The results show that in all three cases the solubility increases with rise of temperature and that the strontium salt is most, and the barium salt least, soluble at the same temperature. The results are tabulated in the original. It is suggested that in the manufacture of tartaric acid this might, with advantage, be precipitated as the barium salt, since this is less soluble than the calcium salt now generally employed. T. A. H.

Thioformic Acid. VICTOR AUGER (*Compt. rend.*, 1904, 139, 798—800).—In order to obtain thioformic acid, the action of sulphide of phosphorus on formic acid, and the saponification of phenyl formate by sodium hydrosulphide have been investigated. Phosphorus pentasulphide has no action on formic acid, even at its boiling point, but sodium metathiophosphate, prepared by fusing 1 mol. of phosphorus pentasulphide with 1 mol. of sodium sulphide, reacts readily. On distilling the product in a vacuum, a mixture of formic and thioformic acids collects in the receiver, from which the formic acid can be separated by cooling to -20°. The remaining liquid is very unstable, gives off hydrogen sulphide, and deposits a white, amorphous substance. Its properties indicate the presence of thio-acid, but this could not be obtained pure.

Phenyl formate reacts readily with sodium hydrosulphide in absolute alcoholic solution, $HCO_2 \cdot C_6H_5 + NaHS = HCO \cdot SNa + C_6H_5 \cdot OH$. After removal of the alcohol, ether precipitates the sodium salt in the form of long, white, very deliquescent needles, which are mixed with excess of formic acid and distilled in a vacuum. The thioformic acid is collected in a receiver cooled by methyl chloride; it decomposes very rapidly.

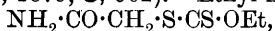
Phenyl formate, which usually contains considerable quantities of

phenol, can be purified by converting the latter into the less volatile phenyl benzoate by means of benzoyl chloride in presence of pyridine, the temperature being kept below 10° , when most of the phenyl benzoate crystallises. Pure phenyl formate boils at 107° under 25 mm. and at 173° under 760 mm. pressure; it solidifies at -45° , is highly refractive, and has a sp. gr. 1.0879 at 0° . H. M. D.

Synthesis of $\beta\beta$ -Dimethyladipic Acid. GUSTAVE BLANC (*Compt. rend.*, 1904, 139, 800—802).—Reduction of $\beta\beta$ -dimethylglutaric anhydride gives a lactone, $\text{CMe}_2\langle\begin{smallmatrix}\text{CH}_2-\text{CO} \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{O}$, which resembles camphor in appearance, melts at 34° , and boils at 234° . When heated with potassium cyanide at 275° and the product hydrolysed, an acid is obtained which most probably is $\beta\beta$ -dimethyladipic acid,
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

It is very soluble in water, insoluble in light petroleum, melts at $87-88^{\circ}$, and is identical with Tiemann's $\beta\beta$ -dimethyladipic acid obtained by the oxidation of α -ionone (compare Abstr., 1898, i, 377). The acid obtained by Noyes (Abstr., 1901, i, 631), by condensing the ethyl ester of γ -bromoisohexoxic acid with ethyl sodiomalonate and hydrolysing the product, which he represented as $\beta\beta$ -dimethyladipic acid, is, on the other hand, only slightly soluble in water, and melts at 102° . The author comes to the conclusion that in Noyes's synthesis an intramolecular change takes place. H. M. D.

Action of Potassium Ethyl Xanthate on Monohalogen Substituted Fatty Acids and their Derivatives. JULIUS TRÖGER and FRANZ VOLKMER (*J. pr. Chem.*, 1904, [ii], 70, 442—448. Compare Cech and Steiner, *Ber.*, 1875, 8, 902).—Ethyl xanthoacetamide,



obtained by the action of chloroacetamide on potassium ethyl xanthate in alcoholic solution, crystallises in glistening leaflets, melts at 114° , and is soluble in alcohol or hot water. Bromine acts towards ethyl xanthoacetamide in neutral or acetic acid solution as an oxidising agent, sulphuric acid being formed.

Ethyl xanthoacetoneitrile, $\text{CN}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$, obtained from potassium ethyl xanthate and chloroacetoneitrile, is a mobile yellow oil, which is soluble in ether or alcohol and is decomposed by hydrogen sulphide in alcoholic ammoniacal solution, or by hydrogen chloride in benzene solution. When heated with hydroxylamine hydrochloride and sodium carbonate in aqueous alcoholic solution, ethyl xanthoacetoneitrile is decomposed with formation of resinous products.

Methyl ethyl xanthoacetate, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, obtained from potassium ethyl xanthate and methyl chloroacetate, is a yellow oil. When shaken with 10 per cent. aqueous ammonia, it dissolves, and on evaporation of the solution yields a white substance, probably a mixture of the amide and the ammonium salt.

Propyl ethyl xanthoacetate, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Pr}$, is a yellow oil, which, when shaken with aqueous ammonia, yields the ammonium salt.

Diethyl xanthoacetate, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, is a mobile, red oil; it is decomposed by the action of phenylhydrazine in alcoholic

solution, but without formation of phenylmethylpyrazoloneketophenylhydrazone (see this vol., i, 89).

Ethyl xantho- α -propionic acid, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, obtained from potassium ethyl xanthate and α -bromopropionic acid, is a green oil. *Ethyl xanthoisobutyric acid* is a mobile yellow oil. *Diethyl xantho- α -butyrate*, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{Et}$, is a viscid, yellow oil. *Ethyl xanthoacetone*, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{Ac}$, is a dark brown oil.

Methyl xanthoacetamide, $\text{OMe}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises in white, glistening scales and melts at 119° . G. Y.

Sulphoisobutyric Acid. J. MOLL VAN CHARANTE (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 275—277).—*Sulphoisobutyric acid*, $\text{SO}_3\text{H}\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$, prepared by the action of sulphuric acid (1 mol.) on isobutyric anhydride (2 mols.), contains $2\text{H}_2\text{O}$ and is very hygroscopic. Its barium salt contains $3\text{H}_2\text{O}$ and its sodium salt $\frac{1}{2}\text{H}_2\text{O}$. By the action of phosphorus pentachloride on the sodium salt, the dichloride may be obtained as a colourless liquid which boils at about 55° under 1—0.5 mm. pressure and solidifies at -10° . It has n_D 1.4887 and the sp. gr. 1.4696 at $20^\circ/4^\circ$. By varying the conditions of the action of phosphorus pentachloride on the sodium salt, a chloroanhydride, melting at 61° , may also be obtained.

With a little water, the dichloride yields *chlorosulphoisobutyric acid*, $\text{SO}_2\text{Cl}\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$, which melts at 134° , whilst with more water sulphoisobutyric acid is produced. By the action of methyl alcohol on the dichloride, *methyl chlorosulphoisobutyrate* is formed; it boils at about 60° under 1.5 mm. pressure and solidifies at 21.5° ; it has the sp. gr. 1.3436 at $20^\circ/4^\circ$ and n_D 1.46658.

The *dimethyl ester*, $\text{SO}_3\text{Me}\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{Me}$, formed from methyl iodide and the normal silver salt, boils at 78 — 82° under 0.5—1 mm. pressure and melts at 4° . It has the sp. gr. 1.2584 at $20^\circ/4^\circ$ and n_D 1.44481.

Methyl sulphoisobutyrate, $\text{SO}_3\text{H}\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{Me}$, prepared by the action of hydrogen chloride and methyl alcohol on sodium sulphoisobutyrate, is hygroscopic. The isomeric hydrogen ester, *methyl-sulphoisobutyric acid*, $\text{SO}_3\text{Me}\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$, melts at 90° . A. McK.

The Aldol from Synthetic isoPropylacetaldehyde [*isoValeraldehyde*]. J. RAINER (*Monatsh.*, 1904, 25, 1035—1050. Compare Kohn, Abstr., 1896, i, 10, 461; 1897, i, 396).—*isoAmyl alcohol* is best prepared by the action of *isobutyl bromide* and magnesium on trioxymethylene in ethereal solution and treatment of the product with water; it boils at 131° and, when oxidised by Lieben's method, yields *isovaleraldehyde* boiling at 90 — 95° . Potassium hydroxide has no action on the aldehyde at the ordinary temperature, but, on careful addition of water so that the temperature is maintained at 20 — 25° , the aldehyde is converted into the aldol; if the temperature is allowed to rise above 30° , the unsaturated aldehyde, $\text{C}_{10}\text{H}_{18}\text{O}$, is formed.

The aldol, $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}(\text{OH})\cdot\text{CHPr}^\beta\cdot\text{COH}$, is formed also by the action of a saturated aqueous solution of potassium carbonate (4 weeks at 10°) on the aldehyde. It crystallises in delicate, white, glistening needles, melts at 83 — 84° , distils unchanged at 110° under 9 mm.

pressure, and, when distilled under atmospheric pressure, decomposes partially into the unsaturated aldehyde and water. When pure, the aldol is stable in air, but if traces of the unsaturated aldehyde are present, or if it is treated with an aqueous alkali hydroxide, or if it is placed over sulphuric acid in a vacuum, it decomposes to a liquid containing the unsaturated aldehyde and its acid. The oxime, $C_{10}H_{20}O:NOH$, is a viscid liquid which boils at 157° under 14 mm. pressure, and decomposes on repeated distillation. The aldol is not acted on by aluminium amalgam or by sodium amalgam in neutral solution; the action of sodium and sulphuric acid or of zinc and acetic acid leads to the formation of the unsaturated aldehyde and its reduction products. When warmed with silver oxide or potassium permanganate and water, the aldol yields traces of valeric acid and the acid, $CH_2Pr^{\beta}\cdot CH(OH)\cdot CHPr^{\beta}\cdot CO_2H$, which crystallises in white needles, melts at $81-82^{\circ}$, distils unchanged at 163° under 18 mm., or with partial decomposition into the unsaturated acid, at $240-244^{\circ}$ under atmospheric pressure; the silver salt, $C_{10}H_{19}O_3Ag$, is crystalline.

The differences, as to the properties of the aldol, between the present results and the statements in the literature are due to previous authors having prepared the aldol from *isovaleraldehyde* obtained from impure *isoamyl* alcohol.

G. Y.

The Condensation Product of Formylisobutyraldol with Acetaldehyde. EDMUND WEIS (*Monatsh.*, 1904, 25, 1065—1072).

—The condensation product, $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot COH$, obtained from acetaldehyde and formylisobutyraldol, does not form an additive compound with bromine. The *oxime*, $C_7H_{15}O_3N$, forms a viscid, yellow oil having an odour of honey; the *diacetyl* derivative, $C_7H_{12}O(OAc)_2$, prepared by boiling the condensation product with acetic anhydride and sodium acetate, is a heavy, yellow oil, which has a pleasant odour and reduces ammoniacal silver solutions.

When reduced with aluminium amalgam in alcoholic solution, the dihydroxyaldehyde yields the *alcohol*, $C_7H_{13}(OH)_3$, which is a viscid, colourless oil, has a bitter flavour, and does not reduce ammoniacal silver solutions.

G. Y.

Phosphorus Acid Derivatives of Ketones and Aldehydes.

CHARLES MARIE (*Ann. Chim. Phys.*, 1904, [viii], 3, 335—432).—The paper is mainly a *résumé* of work already published (compare Abstr., 1901, i, 635; 1902, i, 71, 255, 431, 714; 1903, i, 220, 328, 379, 678; 1904, i, 723, ii, 481), with the following corrections and additions: hydroxyisopropylhypophosphorous acid melts at 52° and not at 45° , its ethyl ester has n_D 1.452 at 18.5° and sp. gr. 1.122 at 22.5° ; the ethyl ester of hydroxyisopropylphosphinic acid boils at 145° under 20 mm. pressure and melts at $14-15^{\circ}$; the acid, $COMePh, H_3PO_2$, obtained by the action of hypophosphorous acid on acetophenone, melts at 85° and not at 70° . Hydroxyisovalerylphosphinic acid, obtained either by the action of phosphorous acid on *isovaleraldehyde* or by oxidising the acid prepared from hypophosphorous acid and the aldehyde, melts at 191° and not at $182-184^{\circ}$, as stated by Fossek (compare Abstr.,

1884, 833); and the acid, $(C_5H_{11}O)_2, H_3PO_2$, obtained as a by-product in the above reaction melts at 230° and not at 160° , as stated by Ville (*Thèse*, Paris, 1890). Hydroxybenzylhypophosphorous acid, obtained by the action of benzaldehyde on hypophosphorous acid, melts at 108° and not at 90° , as stated by Ville, the *silver* salt is white; the *methyl* ester melts at 99° ; and the *benzoyl* derivative at 93° . M. A. W.

A Compound of Mesityl Oxide with Mercuric Chloride. ERNST ERDMANN (*Ber.*, 1904, **37**, 4571—4572. Compare Willstätter and Pummerer, *Abstr.*, 1904, i, 1043).—Mesityl oxide forms a definite additive *compound*, $C_6H_{10}O, HgCl_2$, which is sparingly soluble in mercuric chloride solution. It crystallises from alcohol in colourless needles, has no definite melting point, but sublimes and decomposes when heated.

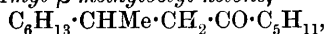
Methylheptenone $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot Ac$, and cineol do not yield similar compounds, whereas cinnamaldehyde gives the *compound* $C_9H_8O, HgCl_2$. J. J. S.

Preparation of α -Substituted β -Ketonic Acids and of Ketones of the Aliphatic Series. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, iii, **31**, 1153—1159. Compare *Abstr.*, 1904, i, 847 and 848).—Ceresole showed (*Abstr.*, 1882, 1052) that the lower members of the substituted acetoacetic esters are readily saponified by agitation with cold potassium hydroxide solution, but this method is inapplicable where the substituting group contains more than C_5 . For the hydrolysis of the higher members of the series, the use of sulphuric acid is now recommended. The ester is rapidly poured into four or five times its weight of sulphuric acid previously heated at from 85 — 95° , and the mixture maintained at this temperature for a few minutes: it is then rapidly cooled and extracted with ether. From the latter, the β -ketonic acid is isolated by agitation with an aqueous solution of sodium carbonate. For the preparation of the ketones, it is unnecessary to isolate the acid first: it is sufficient to pour the sulphuric acid mixture into twice its bulk of water and then distil in a current of steam. A number of ketones were prepared by this process.

The *semicarbazone* of methyl butyl ketone crystallises in spangles from a mixture of light petroleum and alcohol and melts at 127° (corr.), that of methyl hexyl ketone is similar and melts at 122 — 123° (corr.), the corresponding *derivative* of propyl *isobutyl* ketone crystallises in slender needles and melts at 124° (corr.). *Ethyl n-amyl ketone* is a mobile liquid with a fruity odour; it boils at 167 — 168° and yields a *semicarbazone*, crystallising in spangles and melting at 117 — 117.5° (corr.) (compare *Abstr.*, 1903, i, 569). The *semicarbazone* of ethyl *isoamyl* ketone (Ponzio and de Gaspari, *Abstr.*, 1899, i, 252) melts at 132 — 133° (corr.). *Propyl amyl ketone* is a colourless, mobile liquid, boils at 75 — 76° under 10 mm. pressure, and has a sp. gr. 0.837 at $0^\circ/4^\circ$; the *semicarbazone* forms small, white lamellæ and melts at 73 — 74° .

Methyl β -methyloctyl ketone, $C_6H_{13} \cdot CHMe \cdot CH_2 \cdot COMe$, is a mobile liquid with a slight odour of fat: it boils at 115° under 25 mm.

pressure; the *semicarbazone* separates from benzene in colourless crystals and melts at 66°. *Amyl β-methyloctyl ketone*,



is a slightly viscous, colourless liquid with a fatty odour: it boils at 143—144° under 9 mm. pressure and has a sp. gr. 0·845 at 0°/4°.

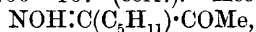
T. A. H.

Preparation of α-Diketone Monoximes of the Type R·CO·CR'·N·OH. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1159—1164. Compare Abstr., 1904, i, 848).—The authors have generalised the process devised by Meyer and Züblin (Abstr., 1878, 487, 659), and improved by Ceresole (Abstr., 1882, 1052, 1883, 41), for the preparation of the monoximes of α-diketones by the action of nitrous acid on α-alkylacetylacetic acids (compare Claisen and Manasse, Abstr., 1887, 944, and 1889, 584; Behr-Bregowski, Abstr., 1897, i, 459; and Ponzio, Abstr., 1897, i, 551).

Ceresole's process is used for the β-ketonic acids soluble in water (that is, members of the series below amylacetoacetic acid). For the acids of the series insoluble in water, it is best to use ether or chloroform as the solvent and nitrosyl chloride or nitrosylsulphuric acid as the generator of nitrous acid. The reaction is carried out at temperatures varying from 0° to 20°, and, when completed, the mixture is poured into a slight excess of sodium carbonate solution, the oxime being obtained by distilling off the solvent and rectifying the residue by distillation under reduced pressure. The yield is from 80 to 95 per cent. The method is, however, only applicable to acids below the term *sec*-octylhexoylacetic acid; the latter, when treated in this way, yields the corresponding ketone mixed with a small quantity of the diketone.

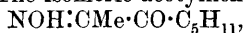
T. A. H.

Oximes and Dioximes of α-Diketones. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1164—1169. Compare preceding abstract).—Diacetylmonoxime semicarbazone melts with decomposition at 303° (corr.) on the mercury-bath or Maquenne block (compare Diels, Abstr., 1902, i, 205). Propionylbutyryloxime, $\text{NOH}\cdot\text{Cet}\cdot\text{COPr}^\alpha$, which was not obtained pure owing to the presence of an impurity in the ethylbutyrylacetic acid used (Locquin, Abstr., 1904, i, 552), boils at 107—108° under 10 mm. pressure (Abstr., 1902, i, 659). *Dibutyryloxime*, prepared from ethyl propylbutyrylacetate, was not obtained pure; the preparation was liquid and boiled at 117—120° under 12 mm. pressure. *Butyrylisobutyryloxime*, $\text{NOH}\cdot\text{CPr}^\beta\cdot\text{COPr}^\alpha$, obtained like the foregoing in an impure state, boiled at 115—119° under 14 mm. pressure. *Propionylisovaleryloxime*, $\text{NOH}\cdot\text{Cet}\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^\beta$, melts at 38—39° and boils at 117—118° under 12 mm. pressure; the corresponding *dioxime* crystallises in translucent lamellæ from alcohol and melts and sublimates at 166—167° (corr.). Acetylhexoyloxime,

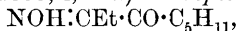


melts at 54° and boils at 133° under 11 mm. pressure (compare Behr-Bregowski, Abstr., 1897, i, 459, and Ponzio and Prandi, Abstr., 1899,

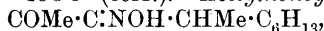
i, 253); the dioxime melts at 173° (corr.) (compare Fileti and Ponzio, Abstr., 1895, i, 499). The isomeric acetylhexoyloxime,



boils at 139° under 16 mm. pressure and melts at 39° (compare Ponzio and de Gaspari, Abstr., 1899, i, 252). *Propionylhexoyloxime*,



forms brilliant, colourless needles, melts at $33\text{--}34^{\circ}$, boils at $131\text{--}132^{\circ}$ under 9 mm. pressure, and is soluble in organic solvents; the corresponding *dioxime* crystallises from boiling benzene in needles and melts and sublimates at $158\text{--}158.5^{\circ}$ (corr.). *Acetylnonoyloxime*,



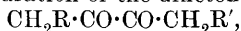
boils at $147\text{--}149^{\circ}$ under 10 mm. pressure, and has a sp. gr. 0.948 at $0^{\circ}/4^{\circ}$; the corresponding *dioxime* is difficult to purify; the *semicarbazone* crystallises from light petroleum and melts at 178° (corr.).

T. A. H.

General Method for the Preparation of α -Diketones. LOUIS BOUEVAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1169—1172. Compare Abstr., 1904, i, 546, 556).—The authors recommend for this purpose the hydrolysis of the diketone monoximes prepared as already described (this vol., i, 19). Von Pechmann's method of hydrolysing these oximes is tedious (Abstr., 1888, 248), and the authors recommend instead the use of nitrous acid, which, as Claisen and Manasse have observed, when used in excess, converts the *isonitroso*-ketones into diketones. Nitrous anhydride, prepared by Lunge's method (Abstr., 1879, 200), is passed into the diketone-oxime for from one to two hours, the temperature being kept below 40° . The product, after being washed with a solution of sodium carbonate, is rectified under reduced pressure. Nitrosylsulphuric acid may also be employed in this reaction as a source of nitrous acid.

T. A. H.

α -Diketones. RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1173—1176. Compare preceding abstract).—The diketones reduce ammoniacal silver nitrate in the cold (compare Petrenko-Kritschenko and Eltschaninoff, Abstr., 1901, i, 506), and with the exception of the higher members readily combine with sodium hydrogen sulphite, even when they do not contain the group $\text{CH}_3\cdot\text{CO}\cdot$. The latter reaction permits of the ready separation of the diketones of the type



where these do not contain more than twelve atoms of carbon, from the mono-ketones of the form $\text{CH}_2\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{R}'$, which are not separable by fractional distillation.

Propionylbutyryl, $\text{CH}_3\text{MeCO}\cdot\text{COPr}$, has an odour like that of diacetyl, boils at $145\text{--}146^{\circ}$, and has a sp. gr. 0.885 at $0^{\circ}/4^{\circ}$ (compare Ponzio and Borelli, Abstr., 1902, i, 659); the dioxime melts at $164\text{--}165^{\circ}$ on the mercury-bath. Dibutyryl boils at $59\text{--}60^{\circ}$ under 12 mm. pressure and at $166\text{--}169^{\circ}$ under 755 mm. pressure, and has a sp. gr. 0.934 at $0^{\circ}/4^{\circ}$; the dioxime crystallises in needles and melts and sublimates at $186\text{--}187^{\circ}$ (corr.) on the mercury-bath (compare Ponzio, Abstr., 1901, i, 452). *Propionylisovaleryl*, $\text{COEt}\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^2$, boils at $59\text{--}60^{\circ}$ under 18 mm. pressure. *Propionylhexoyl*, $\text{COEt}\cdot\text{CO}\cdot\text{C}_5\text{H}_{11}$,

boils, after regeneration from its bisulphite compound, at $77-80^{\circ}$ under 11 mm. pressure, and has a sp. gr. 0.927 at $0^{\circ}/4^{\circ}$. *Acetylnoyol*, $\text{COMe}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{C}_5\text{H}_{11}$, is a mobile liquid with a fatty odour; it boils at 94° under 10 mm. pressure and has a sp. gr. 0.891 at $0^{\circ}/4^{\circ}$.

T. A. H.

Reaction of Aldehydic Sugars. ARMAND BERG (*Bull. Soc. chim.*, 1904, [iii], 31, 1216—1217).—From 0.02 to 0.03 gram of the sugar is added to 10 c.c. of freshly prepared saturated bromine water and warmed for 10 minutes at $60-70^{\circ}$; the bromine is then boiled off, and 10 c.c. of a reagent prepared by adding 4 drops of ferric chloride solution (45° B.) and 2 drops of hydrochloric acid to 100 c.c. of water added. Aldoses under these conditions give an intense yellow coloration, whereas ketoses give no coloration when pure. Commercial sucrose gives a slight yellow colour unless previously recrystallised from alcohol. In applying this reaction to bioses and more complex sugars, care must be taken that the bromine water is free from hydrobromic and other mineral acids.

T. A. H.

A New Sugar from Mountain-Ash Berries. GABRIEL BERTRAND (*Compt. rend.*, 1904, 139, 862—805. Compare Vincent and Meunier, *Abstr.*, 1899, i, 185).—When the sorbite present in mountain-ash berries has been completely converted into sorbose by the action of the sorbose bacterium and the sugar removed by crystallisation, the mother liquor contains a hexahydric alcohol which can be separated in the form of an acetal by treating the syrup with benzaldehyde and sulphuric acid. The syrupy liquid obtained by concentrating the solution resulting from the hydrolysis of the acetal is treated with boiling absolute alcohol; after a time, the solution deposits crystals of the alcohol, *sorbieritol*. The statement of Vincent and Meunier that this alcohol contains eight atoms of carbon is refuted by the author's experiments. *Sorbieritol* melts at 75° , is exceedingly soluble in water, and deliquesces in moist air. Its aqueous solution is laevorotatory; $[\alpha]_D - 3.53^{\circ}$ in 10 per cent. solution at 20° . The analysis of *sorbieritol* and the cryoscopic determination of its molecular weight correspond with the formula $\text{C}_6\text{H}_{14}\text{O}_6$. It yields a hexa-acetyl ester, crystallising from alcohol in hexagonal plates and melting at 123° . In 5 per cent. chloroform solution, $[\alpha]_D 26.66^{\circ}$. With benzaldehyde in presence of sulphuric acid, it gives a mixture of two acetals—a dibenzoic acetal readily soluble in boiling alcohol and melting at 192° , and a tribenzoic acetal much less soluble in alcohol and melting at 240° .

H. M. D.

Synthesis and Chemical Nature of *Sorbieritol*. GABRIEL BERTRAND (*Compt. rend.*, 1904, 139, 983—986).—The author finds that *sorbieritol* (compare preceding abstract) is identical in crystalline form, melting point, and specific rotation with *d*-iditol, prepared together with *d*-sorbitol by the reduction of sorbose in acid solution (compare *Abstr.*, 1898, i, 550), and, further, the acetyl and tribenzoyl derivatives of the two alcohols have the same physical constants. By

taking advantage of the selective oxidising property of the sorbose bacterium (compare Abstr., 1898, 559), it is possible to separate *d*-iditol or synthetical sorbieritol from its isomeride, *d*-sorbitol, in the mixture of the two alcohols obtained by reducing sorbose. The original contains the constitutional formulæ of sorbose, *d*-sorbitol, and *d*-iditol or sorbieritol (compare Fischer and Fay, Abstr., 1895, i, 650).

M. A. W.

Hydrolysis of Sucrose by *d*- and *l*-Camphor- β -sulphonic Acids. ROBERT J. CALDWELL (*Proc. Roy. Soc.*, 1904, 74, 184—187).—So far as the inversion of sucrose is concerned, no difference in the activity of the *d*- and *l*-acids can be detected. The activity of camphor- β -sulphonic acid, as deduced from the sucrose experiments, stands to that of hydrochloric acid in the ratio 89.8:100. When the hydrolysis of milk sugar is made the basis of comparison, the value of the ratio is found to be 70:100.

J. C. P.

***iso*Maltose.** HERMANN OST (*Zeit. angew. Chem.*, 1904, 17, 1663—1670, Compare Grütters, Abstr., 1904, i, 852).—Further evidence is submitted to prove that the *isomaltose*, supposed by Lintner and Düll to be formed as an intermediate product between dextrins and maltose during the hydrolysis of starch, does not exist. E. Fischer's *isomaltose*, formed during the inversion of dextrose by acids, is not identical with Lintner and Düll's product.

In addition to dextrose and dextrins, a considerable amount of maltose was formed as an intermediate product during the hydrolysis of starch by oxalic acid. Lintner and Düll's *isomaltose*, with $[\alpha]_D + 140^\circ$ and a reducing power 80—84 per cent., consists of a mixture of maltose, easily soluble dextrins, and substances which are not sugars. A suitable method of distinguishing between maltose and Fischer's *isomaltose*, which is not fermentable by yeast, is given by the rotation of the corresponding osazones. Maltosazone is strongly dextrorotatory, and the value of its rotation is increased when dextrins are present; Fischer's *isomaltosazone* is levorotatory.

A. McK.

Constitution of Cellulose. II. ARTHUR G. GREEN (*Zeit. Farb. Text.-Ind.*, 1904, 3, 309—310).—A reply to criticisms by Cross and Bevan (Abstr., 1904, i, 652) of a previous paper (*Zeit. Farb. Text.-Ind.*,

3, 97) in which the formula
$$\begin{array}{c} \text{CH(OH)} \cdot \text{CH} \cdot \text{CH(OH)} \\ | \qquad \qquad \qquad \text{>O} \\ \text{CH(OH)} \cdot \text{CH} \text{---} \text{CH}_2 \end{array} \text{O}$$
 for cellulose

was suggested. The determination of the number of acetyl groups in Cross and Bevan's "tetra-acetylcellulose" gave values more closely in agreement with the assumption that this substance is a triacetylcellulose.

W. A. D.

Lignin. VIKTOR GRAFE (*Monatsh.*, 1904, 25, 987—1029).—Lignin consists principally of vanillin, methylfurfuraldehyde, catechol, and coniferin in ethereal combination with cellulose. On hydrolysis of the cellulose ethers with dilute acids or alkali hydroxides, furfuraldehyde is formed from the pentoses of the wood; this is avoided by hydrolysis

with water at 180° in a vacuum, or by electrolysis in warm water under pressure. Vanillin is found also in the sulphite mother liquors obtained in the commercial preparation of cellulose.

Wiesner's and Mäule's reactions take place with the phenolic components of lignin, and, as methylfurfuraldehyde and catechol can be formed simply from cellulose, cannot be used as tests for its presence. The blue coloration obtained by the action of phenol, hydrochloric acid, and potassium chlorate on wood is to be ascribed to the presence of coniferin, and the green coloration with hydrochloric or hydrobromic acid to methylfurfuraldehyde in combination with coniferin. The intensity of the colour reactions of wood is due to the sensitiveness of the phenol dyes, to the finely divided state in which these are distributed through the substance, and to the manner in which cellulose retains substances which have permeated it.

Methoxyl determinations show lignin to contain 48 per cent. of vanillin if that is the only methoxy-compound present. Vanillin, methylfurfuraldehyde, and catechol constitute the so-called hadromal, the chromogen of lignin. G. Y.

Choline, Neurine, and Allied Compounds. ERNST A. SCHMIDT (*Annalen*, 1904, **337**, 37—121. Compare Abstr., 1892, 905).—A study has been made of the derivatives of choline, neurine, and muscarine, mainly with the object of ascertaining the variation of physiological action with change of constitution.

In the case of neurine, addition of alkyl groups not only weakens the physiological action, but also alters its character; it is remarkable, however, that trimethylneurine is more active than the dimethyl derivative.

Natural muscarine ("pilzmuscarin"), when compared with the artificial muscarines, cholinemuscarine, or ψ -muscarine from Prussian blue, is physiologically inactive. On comparing the behaviour of homoisomuscarine with that of isomuscarine, it was found, as in the case of the neurines, that lengthening of the side-chain reduces the physiological activity.

When choline is converted into the ethyl or methyl ether, $\text{OH} \cdot \text{NMe}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OEt}$, it is found that the toxic action was markedly increased.

[With WALDEMAR WAGNER.]—Bromine only attacks choline when they are heated together under pressure at 120 — 130° ; the product, a perbromide, is converted by boiling with alcohol into trimethylbromoethylammonium bromide, $\text{C}_2\text{H}_4\text{Br} \cdot \text{NMe}_3\text{Br}$, which forms colourless crystals melting at 230° ; the *platinichloride*, $(\text{C}_2\text{H}_4\text{Br} \cdot \text{NMe}_3)_2\text{PtCl}_6$, prepared by decomposing the bromide with silver chloride and adding platinic chloride, forms octahedral crystals melting at 240° . The *aurichloride* forms prismatic crystals melting at 222 — 223° . On treatment with moist silver oxide, the bromide is converted into neurine.

Choline chloride is only attacked by sulphuric acid at 100° , a sulphate being obtained which is identical with that formed on treating trimethylbromoethylammonium bromide with silver sulphate; it has therefore the formula $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{SO}_3 \\ | \\ \text{NMe}_3 \cdot \text{O} \end{smallmatrix}$; it crystallises in white

leaflets and decomposes without melting. No dehydration with the production of neurine appeared to occur.

Attempts to convert choline into neurine by the action of phosphorus oxychloride or zinc chloride failed; the substance first mentioned led to the production of a salt which yielded the *platinichloride*, $(C_2H_4Cl \cdot NMe_3Cl)_2PtCl_6$, a compound crystallising in octahedra and not melting at 250° ; the *aurichloride* crystallises in needles melting at 239° .

Choline is converted by nitric acid into nitrosocholine, the *platinichloride* of which, $(NO \cdot O_2 \cdot C_2H_4 \cdot NMe_3)_2PtCl_6$, is anhydrous and does not crystallise with $2H_2O$, as Nothnagel states (*Arch. Pharm.*, 1904, 284). The *aurichloride* crystallises in groups of needles melting at 234° . The formation of cholinemuscarine was not observed.

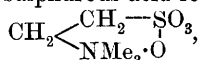
The ethers of choline are not produced either by the action of methyl iodide and sodium methoxide on choline chloride or by the action of sodium methoxide on trimethylbromoethylammonium bromide, but can be easily obtained by the action of methyl bromoethyl ether or bromoethyl ether on trimethylamine. The *iodide* of choline methyl ether, $OMe \cdot CH_2 \cdot CH_2 \cdot NMe_3I$, is prepared from iodoethyl methyl ether and 33 per cent. trimethylamine, and crystallises in hygroscopic needles. The *platinichloride* crystallises in yellowish-red needles melting at $216-217^\circ$, and the *aurichloride* in yellow needles melting at 156° . The corresponding *bromide*, prepared in a similar manner, crystallises in hygroscopic needles; it was converted into the corresponding *chloride*, which yielded with excess of mercuric chloride the double salt, $C_2H_4(OH) \cdot NMe_3Cl \cdot 6HgCl_2$; the latter forms crystals melting at 205° .

The corresponding ethyl ether of choline, $OEt \cdot C_2H_4 \cdot NMe_3Br$, is prepared from bromoethyl ether and trimethylamine, and forms crystals melting at 175° . The *platinichloride* forms reddish-yellow prisms melting at 243° , and the *aurichloride* needles or leaflets melting at 140° .

Bromoethyl ether combines with pyridine in a similar manner, yielding the compound $OEt \cdot C_2H_4 \cdot C_5NH_5Cl$, which could not be isolated, but which was converted into an *aurichloride*, crystallising in small needles.

[With WALDEMAR WAGNER.]—An attempt was made to convert neurine into choline by the addition of the elements of water effected by repeated evaporation of the nitrate with dilute nitric acid; very little of the neurine was changed, but traces of choline and nitrosocholine were found in the product.

Neurine combines with sulphurous acid forming *taurobetaine*,



which forms crystals insoluble in alcohol and not molten at 250° .

Attempts to convert neurine into *isomuscarine* by oxidation with 1 per cent. permanganate in neutral solution did not give the desired result; the neurine was mainly unchanged, a small quantity of trimethylamine being also formed. Treatment of neurine dibromide with silver nitrate with the object of obtaining *isomuscarine* led only to the production of a small quantity of *trimethylbromovinylammonium chloride*, $CHCl : CH \cdot NMe_3Cl$, the *platinichloride* of which

crystallised in leaflets melting at 201° , and the *aurichloride* in yellow prisms melting at 210° .

Neurine was not reduced either by zinc and sulphuric acid or by sodium amalgam.

[With FRANZ M. LITTERSCHEID.]—The action of methylene iodide on trimethylamine, by which Hofmann prepared trimethyliodomethylammonium salts, depends greatly on the conditions. At a low temperature, trimethyliodomethylammonium salts are formed; the *platinichloride* crystallises in needles or leaflets, becoming brown at 215° and melting and decomposing at 235° , and the *aurichloride* in yellow needles melting at 249° , and the *mercurichloride* in needles melting at 174 – 175° . The *base* is a crystalline, hygroscopic mass, and the chloride forms hygroscopic plates melting at 178 – 179° , and the *picrate* long, yellow needles melting at 196° . When trimethylamine and the iodide are heated under pressure for 1 hour, the same products are obtained as at the ordinary temperature. After 2 hours' heating, tetramethylammonium salts are also formed, the *aurichloride* crystallising in needles not melting at 250° . After 4 hours' heating, the tetramethylammonium iodide is the only solid, the liquid containing, besides formaldehyde, the iodide of a *base* melting at 207 – 208° , the *aurichloride* of which melts at 140° . When trimethyliodomethylammonium iodide is heated with trimethylamine under pressure, the same products are obtained, showing that on heating methylene iodide with trimethylamine, the base, trimethyliodomethylamine, first formed reacts with the excess of trimethylamine. Ammonia does not react with trimethyliodomethylammonium iodide.

Trimethylbromomethylammonium bromide, $\text{CH}_2\text{Br}\cdot\text{NMe}_3\text{Br}$, prepared from trimethylamine and methylene bromide, forms large, flat crystals melting at 160° ; the *platinichloride*, $(\text{CH}_2\text{Br}\cdot\text{NMe}_3\text{Br})_2\text{PtCl}_4$, forms red, octahedral crystals blackening and melting at 208° , whilst the *platinichloride*, $(\text{CH}_2\text{Br}\cdot\text{NMe}_3)_2\text{PtCl}_6$, forms yellow, octahedral crystals melting at 199° . The base forms a hygroscopic, crystalline mass, which is converted into the carbonate when exposed to the air.

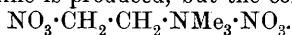
[With FRANZ M. LITTERSCHEID.]—Formocholine (*trimethylhydroxymethylammonium hydroxide*), $\text{OH}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$, forms a crystalline, hygroscopic mass; the *platinichloride* crystallises in readily soluble octahedra melting and decomposing at 230° , and the *aurichloride* in slender, yellow needles, which do not melt at 250° . The *mercurichloride* forms plates not melting at 250° . Attempts to acetylate and benzoylate formocholine by heating the chloride with acetyl chloride or benzoyl chloride only lead to the formation of tetramethylammonium salts. Attempts to prepare formocholine by heating trimethylbromomethylammonium bromide with water under pressure only resulted in complex decomposition.

[With WALDEMAR WAGNER.]—On reducing trimethylbromoethylammonium bromide either with sodium amalgam or zinc and sulphuric acid, trimethylamine is formed.

When the bromide is heated with a solution of silver sulphate for 2 days, the compound, $\text{CH}_2\text{<}\begin{matrix} \text{CH}_2-\text{SO}_3 \\ \text{NMe}_3\cdot\text{O} \end{matrix}$, is obtained as a white, crystal-

line powder or leaflets, which give no precipitate with barium until boiled with hydrochloric acid. In this reaction, a small portion of trimethylbromoethylammonium salts and choline are produced.

When trimethylbromoethylammonium bromide is boiled with alcoholic silver nitrate, no choline is produced, but the compound

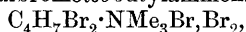


From it a *platinichloride*, $(\text{NO}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_3)_2 \text{PtCl}_6$, is obtained in reddish-yellow, soluble crystals melting at $227-228^\circ$; the *aurichloride* forms soluble needles melting at 133° .

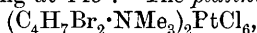
[With G. KLEINE.]—Ethylene bromide and trimethylamine react together at the ordinary temperature, giving trimethylbromoethylammonium bromide, but, when heated together under pressure at 100° , there are also produced tetramethylammonium bromide, hexamethylethylenediamine bromide, neurine bromide, trimethylamine hydrobromide, and dimethylamine hydrobromide, together with aldehyde and aldehyde resin. The *platinichloride* of hexamethylethylenediamine, $\text{C}_2\text{H}_4(\text{NMe}_3)_2 \text{PtCl}_6$, crystallises in small, pale orange plates, becoming black at 260° and melting at $275-276^\circ$; the *aurichloride* crystallises in golden-yellow leaflets melting at $223-225^\circ$.

When propylene bromide and trimethylamine were heated together for 6 hours at 100° in alcoholic solution, α -bromopropylene, trimethylamine, and dimethylamine hydrobromide and trimethylpropenylammonium bromide, $\text{C}_3\text{H}_5 \cdot \text{NMe}_3 \cdot \text{Br}$, are formed. The *platinichloride* of the propenyl derivative, $(\text{C}_3\text{H}_5 \cdot \text{NMe}_3)_2 \text{PtCl}_6$, crystallises in dark orange-red scales melting and decomposing at 249° ; the *aurichloride* forms yellow needles melting at $199-202^\circ$.

*iso*Butylene bromide reacts with trimethylamine in alcoholic solution both at the ordinary temperature and at 100° with the production of *isocrotyl* bromide and trimethylamine hydrobromide. The *isocrotyl* bromide combines to a small extent with trimethylamine, forming *trimethylisocrotylammonium bromide*, which was isolated as a *platinichloride*, $(\text{C}_4\text{H}_7 \cdot \text{NMe}_3)_2 \text{PtCl}_6 \cdot \text{H}_2\text{O}$, which crystallises in long, orange leaflets melting at $206-207^\circ$; the *aurichloride* forms large, golden-yellow needles melting at $190-191^\circ$. Experiment showed that *isocrotyl* bromide would not combine directly with trimethylamine. The *perbromide* of trimethyldibromoisobutylammonium bromide,



is obtained in reddish-brown crystals when the *isocrotyl* salt is treated with bromine in chloroform solution; on boiling with alcohol, it is converted into *trimethyldibromoisobutylammonium bromide*, which crystallises in leaflets melting at 145° . The *platinichloride*,



crystallises in orange-red scales melting at $212-213^\circ$. The *aurichloride* forms needles melting at 145° . When treated with moist silver oxide, *trimethylbromoisocrotylammonium hydroxide* is produced, and yields the *platinichloride*, $(\text{C}_4\text{H}_7\text{Br}_2 \cdot \text{NMe}_3\text{Cl})_2 \text{PtCl}_4$, which forms orange, star-shaped groups of needles melting at $203-204^\circ$, and an *aurichloride* which crystallises in lemon-yellow needles melting at 126° .

ψ -Butylene bromide interacts with trimethylamine in alcoholic solution both at the ordinary temperature and at 100° , yielding trimethylamine hydrobromide, ψ -crotyl bromide, the bromide of hexamethyl- ψ -

butylenediamine; the *platinichloride*, $C_4H_8(NMe_3)_2PtCl_6$, forms crystals melting at $221-222^\circ$. On attempting to form the aurichloride, a decomposition took place, the *aurichlorides* of trimethyl- ψ -crotylammonium chloride, $C_3H_7 \cdot NMe_3 \cdot AuCl_4$, a substance melting at 175° , and of trimethylamine hydrochloride were obtained.

Amylene bromide and trimethylamine were brought together in alcoholic solution and heated at 100° ; the main product is *trimethylpentenylammonium bromide*, the *platinichloride* obtained from which crystallises with H_2O , and the *aurichloride* in small needles melting at 193° . At the same time, a small amount of *hexamethylamylenediammonium bromide* is produced; the *platinichloride*, $C_5H_{10} \cdot (NMe_3)_2PtCl_6$, crystallises in needles melting at 203° ; it could not be converted into a gold salt, as trimethylamine is eliminated and valeryltrimethylammonium chloride produced. *Trimethylpentenylammonium bromide* readily forms the *perbromide*, $C_5H_9Br_2 \cdot NMe_3Br, Br_8$, which is decomposed by alcohol.

[With HILDERICH HARTMANN.]—Trimethylglycerylammonium chloride, prepared by Meyer and Scholten's method from α -monochlorhydrin and trimethylamine, yields a dibenzoate when heated with benzoic anhydride; the *platinichloride*, $[C_3H_5(OBz)_2 \cdot NMe_3]_2PtCl_6$, is a red solid melting at 191° . The glycerylammonium salt is converted by red phosphorus and hydriodic acid into the compound $C_3H_5I_2 \cdot NMe_3I$, which forms leaflets; in the mother liquor, another base is contained, and can be isolated as an *aurichloride*, $OH \cdot C_3H_5I \cdot NMe_3 \cdot AuCl_4$, crystallising in yellow leaflets melting at 101° ; the *platinichloride* crystallises in reddish-brown needles, becoming black at 176° and melting and decomposing at 194° .

When oxidised with nitric acid, a compound is formed which can be isolated as *platinichloride*, $[CO_2H \cdot CH(OH) \cdot CH_2 \cdot NMe_3]_2PtCl_6$, crystallising in yellowish-red tetrahedra melting at 233° ; the *aurichloride* forms lemon-yellow crystals melting at 172° . It is suggested that this compound is possibly not a hydroxyhomobetaine, but a hydroxyhomomuscarine, $CH(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NMe_3Cl$.

As regards the interaction of α -dichlorohydrin and trimethylamine, the results of other observers are confirmed.

β -Dibromohydrin and trimethylamine react either at the ordinary temperature or at 100° with the elimination of hydrobromic acid; at the same time, hexamethylhydroxypropylenediammonium bromide is formed and isolated as *platinichloride*, $OH \cdot C_3H_5(NMe_3)_2PtCl_6$, which crystallises in needles blackening at 256° and melting and decomposing at 263° ; the *aurichloride* is a yellow, crystalline precipitate melting at $242-244^\circ$.

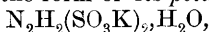
β -Dichlorohydrin behaves with trimethylamine as does the bromohydrin.

Allyl tribromide and trimethylamine are found to react in the manner described by Partheil (Abstr., 1890, 356), trimethylbromoallylammonium bromide and trimethylamine hydrobromide being formed.

Epichlorohydrin and trimethylamine readily react in the cold; on heating the mixture for six hours under pressure, trimethylhydroxypropylammonium bromide is the main product, the direct additive product of epichlorohydrin and trimethylamine being at the same time

produced; it was found to be identical with Partheil's anhydrohomoisomuscarine (*loc. cit.*).
K. J. P. O.

Hydrazinecarboxylic Acid. ROBERT STOLLÉ and K. HOFMANN (*Ber.*, 1904, 37, 4523—4524).—On passing a current of carbon dioxide into a well-cooled concentrated aqueous solution of hydrazine, *hydrazinecarboxylic acid*, $\text{NH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{H}$, separates as a white powder, which may be dried over sulphuric acid in an atmosphere of carbon dioxide. It partially decomposes at 90° into carbon dioxide and *hydrazine hydrazinecarboxylate*, $\text{NH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{H}, \text{N}_2\text{H}_4$, which distils at 140° under the ordinary pressure, or at 75° under 23 mm. pressure as a clear, viscous liquid, slowly solidifying to a crystalline mass when kept over sulphuric acid, and then melting at about 70° . It dissolves very readily in water to an alkaline solution, but is rapidly decomposed by acids, and is partially decomposed to carbonylhydrazide on heating at 140° in a closed tube. With ethyl chlorosulphonate it yields *hydrazinedisulphonic acid*, which may be isolated in the form of its *potassium salt*,



crystallising from water in transparent prisms. The acid yields no condensation product with benzaldehyde.

Hydrazinemonosulphonic acid is also formed in the above reaction, and may be isolated in the form of potassium benzyldenedehydrazinesulphonate.

Hydrazinecarboxylic acid and its hydrazine salt may be employed in many reactions in place of anhydrous hydrazine. The latter may also be prepared from them by distillation with calcium or barium oxide. An accidental explosion once occurred during the final distillation.
C. H. D.

Some Substances of Physiological Importance. MARTIN SCHENCK (*Zeit. physiol. Chem.*, 1904, 43, 72—73).—*Guanidine cadmium chloride*, $\text{CH}_5\text{N}_3\text{HCl} \cdot 2\text{CdCl}_2$, obtained in the form of a voluminous precipitate by mixing concentrated alcoholic solutions of guanidine chloride and cadmium chloride, melts at 390 — 395° .

Biuret cadmium chloride, $(\text{C}_2\text{H}_5\text{O}_2\text{N}_3)_2, \text{CdCl}_2$, melts and decomposes at 255 — 260° and is only sparingly soluble in hot ethyl alcohol.

Histidine cadmium chloride, $\text{C}_6\text{H}_9\text{O}_2\text{N}_3\text{HCl} \cdot \text{CdCl}_2$, melts and decomposes at 270 — 275° and is practically insoluble in hot ethyl alcohol. All three compounds are readily soluble in water.

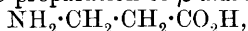
A compound of *arginine*, $(\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4)_2, \text{Cu}(\text{NO}_3)_2, 2\text{H}_2\text{O}$, melting at 226° , has also been prepared.
J. J. S.

Diaminoguanidine. ROBERT STOLLÉ and K. HOFMANN (*Ber.*, 1904, 37, 4524—4525. Compare *Abstr.*, 1904, i, 980).—Anhydrous hydrazine reacts with cyanogen chloride in cooled ethereal solution to form *diaminoguanidine hydrochloride*, $\text{CH}_7\text{N}_5\text{HCl}$, a white powder melting at 174° , and dissolving readily in water to a neutral solution which reduces ammoniacal silver nitrate. Cyanohydrazine is first formed, which then combines with a second molecule of hydrazine.

Diaminoguanidine hydrochloride reacts with benzaldehyde to form *dibenzylidenediaminoguanidine hydrochloride*, $\text{C}_{15}\text{H}_{15}\text{N}_5\text{HCl}$, crystal-

lising from alcohol in pale yellow needles melting at 232° . The *base* crystallises from alcohol in yellow needles melting at 176° , insoluble in water, readily soluble in ether. C. H. D.

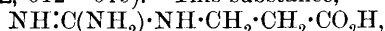
β -Alanine. F. H. HOLM (*Arch. Pharm.*, 1904, **242**, 590—612).—Various methods for the preparation of β -alanine,



have been examined. The conclusion drawn is that this substance is best prepared by the action of alkaline potassium hypobromite on succinimide (Hoogewerff and van Dorp, *Abstr.*, 1891, 1216), as this method is the quickest, and at once gives a pure product; the yield is 60 per cent. of the theoretical.

β -Alanine melts at 196° ; when heated for some time at this temperature, it decomposes for the most part into ammonia and acrylic acid. The *hydrobromide* melts at 105 — 115° , the *hydriodide* at 199° , the *aurichloride* at 144 — 145° , the *platinichloride* at 210° ; the copper salt, with $6\text{H}_2\text{O}$, and *silver* salt, melting at 130° , were analysed. The *aurichloride* of the *ethyl* ester, melting at 143 — 146° , and *platinichloride* and *aurichloride* of the *methyl* ester, the former melting at 192° , the latter very deliquescent, were prepared for the first time. The *benzoyl* derivative melts at 120° and forms a *silver* salt which melts at 240° . C. F. B.

β -Alacreatine (β -Guanidopropionic Acid). F. H. HOLM (*Arch. Pharm.*, 1904, **242**, 612—619).—This substance,



was prepared from cyanamide and β -alanine (Mulder, this Journal, 1877, ii, 311). The hydrochloride, melting at 140° , is anhydrous; the *platinichloride* and *aurichloride* melt at 184° and 130 — 133° respectively.

When β -alacreatine is heated with fuming hydrochloric acid at 125 — 130° for 8 hours in a sealed tube, the *hydrochloride* of β -alacreatinine, $\text{NH}:\text{C} \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \text{NH} - \text{CO} \end{smallmatrix} \text{CH}_2$, is formed; this melts at 268 — 271° , the *platinichloride* at 220° , the *aurichloride* at 202° . When a solution of the hydrochloride is digested with lead oxide and the liquid freed from lead by means of hydrogen sulphide, the filtrate has a strong alkaline reaction at first, but this soon disappears, and β -alacreatine crystallises out; evidently β -alacreatinine itself is a very unstable substance, and rapidly takes up water, forming β -alacreatine. C. F. B.

Glycocyamine and Glycocyamidine. GEORG KORNDÖRFER (*Arch. Pharm.*, 1904, **242**, 620—640).—The glycocyamine (guanineacetic acid), $\text{NH}:\text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, obtained from guanidine carbonate and glycine, is identical with that from cyanamide and glycine; the former method of preparation is the more convenient. The *platinichloride* crystallises with $2\text{H}_2\text{O}$; an *aurichloride*, melting at 173° , with the anomalous composition $2\text{C}_3\text{H}_7\text{O}_2\text{N}_3 \cdot \text{HAuCl}_4$ was obtained; the copper salt is only obtained constant in composition by precipitating a hot copper solution with a cold solution of glycocyamine and heating

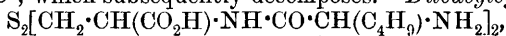
the precipitate for half an hour at 100°. The solubility of glycoeyamine in water is variable, but is apparently about 1 part in 230. When boiled with aqueous barium hydroxide, glycoeyamine is hydrolysed to ammonia, carbon dioxide, glycine (a *sulphate* of which, containing 11·7 per cent. of SO₃, was obtained), and hydantoic acid (which melts at 171—173°).

Glycoeyamidine, $\text{NH}\cdot\text{C} \begin{smallmatrix} \text{NH}\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, is best obtained by heating glycoeyamine at 160—170° (at a slightly higher temperature, further decomposition occurs). Instead of the normal aurichloride, a *compound*, C₃H₅ON₃·AuCl₃, was obtained; the *monosilver* derivative was also analysed. When glycoeyamidine is heated with methyl iodide in methyl-alcoholic solution at 100°, it is converted into a *methiodide* which does not melt below 245°; the *methochloride* also is unmelted at 245°, and so is the *platinichloride*, which crystallises with 2H₂O; the *aurichloride* melts at 168°, the *picrate* at 193°, decomposition beginning at 180°. These salts are not identical with those of creatinine having the same composition (*creatinine hydriodide* melts at 194—195°). As they are hydrolysed by aqueous barium hydroxide to ammonia, methylamine, glycine, and hydantoic acid, they must be regarded as salts of δ -methylglycoeyamidine, NMe·C $\begin{smallmatrix} \text{NH}\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$. When the iodide is treated with silver hydroxide, an alkaline solution is obtained at first, but this gradually becomes feebly acid, and it is then methylglycoeyamine, not methylglycoeyamidine, that is present in the solution.

C. F. B.

Synthesis of Polypeptides. VII. Derivatives of Cystine.

EMIL FISCHER and UMETARO SUZUKI (*Ber.*, 1904, **37**, 4575—4581. Compare Abstr., 1903, i, 465, 607, 799; this vol., i, 652, 771, 867, 890).—Cystine combines with two molecules of acid chlorides containing halogen in alkaline solution forming crystalline products, which, when acted on by ammonia, are converted into the corresponding polypeptide derivatives. *Dichloroacetylcystine*, prepared from cystine and chloroacetyl chloride, crystallises in microscopic, colourless prisms or plates, melting to a colourless oil at 134·5—136·5° (corr.). *Diglycylcystine*, S₂[CH₂·CH(CO₂H)·NH·CO·CH₂·NH₂]₂, separates as a colourless, transparent, amorphous mass, which dissolves copper oxide with a blue coloration. *Dibromopropionylcystine*, prepared by the interaction of cystine and bromopropionyl bromide, crystallises from a mixture of ethyl acetate and ether in long needles which sinter at 60°. The dry substance melts at 145·5—146·5° (corr.) to a brown oil and subsequently decomposes. *Dialanylcystine*, S₂[CH₂·CH(CO₂H)·NH·CO·CHMe·NH₂], forms stellate aggregates of microscopic prisms, which become coloured at 215° and decompose on further heating. In normal hydrochloric acid, it has [α]_D - 192·8° at 20°. *Di- α -bromoisohexoylcystine*, prepared from α -bromoisohexoyl chloride and cystine, crystallises in microscopic, glistening, colourless prisms; these begin to sinter at 120° and gradually melt to an oil at 135°, which subsequently decomposes. *Dileucylcystine*,

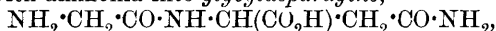


is an amorphous substance sintering at 178°.

Inasmuch as cystine is stereochemically similar to active tartaric acid, three isomeric optically active products can be formed with a racemic acid chloride, which can be represented as *dd*, *ll*, and *dl*. In general, the combinations *dd*, *ll* will be formed in equal amounts, but the amount of the combination *dl* is independent of the amount of these and it may even be the sole product. In the case of dibromopropionylcystine, the product appears to be homogeneous and to represent, therefore, the *dl* form.

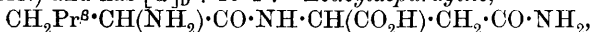
E. F. A.

Synthesis of Polypeptides. VIII. Chlorides and Amides of Aspartic Acid. EMIL FISCHER and ERNST KOENIGS (*Ber.*, 1904, 37, 4585—4603).—*Chloroacetylaspargine*, prepared by the condensation of *l*-aspargine with chloroacetyl chloride in presence of sodium hydroxide, crystallises in needles melting at 148—149° (corr.) and is converted on heating with ammonia into *glycylaspargine*,



which crystallises in needles, melting and decomposing at 216° (corr.) and has $[\alpha]_D - 6.4^\circ$ at 20°. *Ethyl chloroacetylaspargate*, prepared by treating ethyl *l*-aspartate with chloroacetyl chloride in presence of sodium carbonate, crystallises in long needles melting at 46—47°; heating with strong alcoholic ammonia converts it into *anhydroglycylaspargine*, probably $\text{CH}_2 \cdot \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, which crystallises in needles, and on heating turns brown at 245° (corr.) and decomposes at 274° (corr.). *Ethyl anhydroglycylaspargate*, crystallises in well formed leaflets melting at 211—212° (corr.).

α -Bromoisohexylasparginè is formed as a mixture of two isomerides from *l*-aspargine and *α -bromoisohexoyl chloride*. These are separable by fractional crystallisation from water, the sparingly soluble portion crystallising in long, narrow prisms melting at 178° (corr.) and having $[\alpha]_D - 25.6^\circ$ at 20°, whilst the more soluble isomeride melts at about 148° (corr.) and has $[\alpha]_D + 15.4^\circ$. *Leucylaspargine*,



prepared by the action of aqueous ammonia on this mixture of isomerides, crystallises with 2H₂O in flat prisms melting at 195° (corr.), the anhydrous form melting and decomposing at 230° (corr.). *Ethyl α -bromoisohexylaspartate* crystallises in long, fine leaflets melting at 61—62° (corr.); the corresponding acid separates in colourless, crystalline aggregates which melt at 152—154° (corr.). *Leucylaspartic acid*, $\text{CH}_2\text{Pr}^S \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, formed from the foregoing by the prolonged action of aqueous ammonia, crystallises with 1H₂O and melts and decomposes at 180—182° (corr.). *Diethyl fumaryldiglycine*, prepared by condensing fumaryl chloride with ethyl glycine in cold ethereal solution, melts at 211° (corr.); on hydrolysis with sodium hydroxide, it yields *fumaryldiglycine*,



crystallising in colourless, oblique, four-sided plates melting and decomposing at 290° (corr.). On heating with aqueous ammonia for four hours under pressure at 100°, inactive *asparagylmonoglycine* is formed. This separates from water in tiny crystals and melts at 148° (corr.); boiling with hydrochloric acid converts it into glycine and *i*-aspartic

acid. *Diethyl fumaryldialanine* melts at 203—205° (corr.); *fumaryl-alanine* separates in microscopic rhombs melting and decomposing at 275° (corr.). *Aspartyldialanine*,

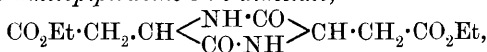


prepared by the action of ammonia on fumaryldialanine, crystallises with 2H₂O and melts at 115° (corr.), solidifies to a mass of fine leaflets and melts again at 150° (corr.).

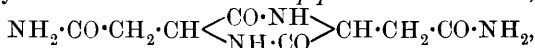
Ethyl fumaryldiaspartate, prepared by the interaction of fumaryl-chloride with much ethyl aspartate, melts at 195°. *Chlorosuccinyldialanine*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared from alanine and chlorosuccinyl chloride, crystallises in long prisms melting and decomposing at 210° (corr.).

Diethyl aspartate is conveniently prepared by the action of hot alcohol saturated with dry hydrogen chloride on asparagine. When exposed to the action of anhydrous liquid ammonia, it is converted into a mixture of aspartic diamide and asparaginimide. *Aspartic diamide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}_2$, melts at 131°, reacts strongly alkaline, and gives a brilliant biuret coloration; characteristic salts could not be prepared. In methyl-alcoholic solution it has $[\alpha]_D$ about -7°.

Ethyl 2:5-diketopiperazine-3:6-diacetate,



is best prepared by boiling ethyl aspartate in presence of a small quantity of zinc chloride for 48 hours: it crystallises in colourless needles melting at 179—180° (corr.). The ester is hydrolysed by dilute barium hydroxide and the solution gives a precipitate with silver nitrate, probably the *silver* salt of the acid. This ester is converted by liquid anhydrous ammonia into *diketopiperazinediacetamide*,

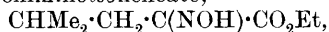


identical with the asparaginimide described by Körner and Menozzi (Abstr., 1887, 1031); the formula $\text{NH}_2\cdot\text{CH}\begin{matrix} \text{CO}\cdot\text{NH} \\ \text{CH}_2\cdot\text{CO} \end{matrix}$, deduced by these authors, should therefore be doubled. E. F. A.

Reduction of α -Oximino-esters; Synthesis of Homologues of Glycine and their Esters. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1176—1180).—The α -oximino-esters may be conveniently reduced to the corresponding α -amino-esters by reduction with either aluminium amalgam or sodium amalgam. In both processes there is formed, in addition to the amino-ester and amino-acid, a small quantity of the ester of the corresponding hydroxy-acid. The reduction of α -oximino-esters to the corresponding amino-esters by aluminium amalgam is somewhat unexpected in view of Bouveault and Wahl's observation that the α -nitroethylenes are converted by this reagent into aldoximes. The further reduction in the present case appears to be due to the influence of the carboxyethyl-group (compare Abstr., 1901, i, 114). When ethyl oximinoisobutylacetate, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{Et}$, is reduced with aluminium amalgam, there is formed some *ethyl α -hydroxyisohexoate*; this is

a colourless, oily liquid, which boils at 82° under 10 mm. pressure and has a sp. gr. 0.9832 at $0^{\circ}/4^{\circ}$. T. A. H.

New Synthesis of Racemic Leucine. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1904, [iii], 31, 1180—1183. Compare preceding abstract).—*Ethyl α -aminoisohexanoate*, produced by the reduction of ethyl α -oximinoisohexanoate,



is a colourless, mobile liquid with a disagreeable odour: it boils at 94° under 16 mm. pressure, has a sp. gr. 0.9765 at $0^{\circ}/4^{\circ}$, and when treated with potassium cyanate furnishes the corresponding *carbamide*, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{Et}$, which crystallises in white needles from a mixture of ether and light petroleum and melts at 92 – 93° . On prolonged ebullition with water, the ethyl ester yields the corresponding acid (formed also in the reduction of the oximino-ester), which is identical with *r*-leucine. The synthetic material melted at 290° , the benzoyl derivative at 139 – 440° (corr.), the benzenesulphonate at 145 – 146° (corr.), and the 2:5-diketo-3:6-diisobutylpiperazine (leucinimide), produced by spontaneous change of the ethyl ester, at 265° . These melting points were determined on the Maquenne block and differ slightly from those recorded by Schulze and Likiernik (*Abstr.*, 1891, 681; 1893, i, 309) and Fischer (*ibid.*, 1900, i, 646). T. A. H.

Preparation of Crystallised Taurocholic Acid. OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1904, 43, 127—144).—Crystallised taurocholic acid may be obtained by the following process. A 2 per cent. aqueous solution of the sodium salt is mixed with a 2 per cent. solution of hydrochloric acid, then saturated with sodium chloride, filtered if necessary, and mixed with ether and shaken, when crystals begin to appear after several hours. A simpler method is to dissolve the taurocholate in alcohol containing a little water, acidify with hydrochloric or sulphuric acid, filter, and then add ether to the filtrate until a marked opalescence is observable. The presence of a small amount of water is absolutely necessary, as otherwise the acid is deposited in an amorphous condition. After several solutions in alcohol and precipitations with ether, the acid is obtained free from mineral matter. The acid obtained from different biles has the same properties. It crystallises in long needles or large prisms, has a characteristic sweet taste, is readily soluble in water or alcohol, but is insoluble in ether, benzene, or acetone, and is not deliquescent. When heated at 100° , it gradually decomposes.

Details are given for the extraction of taurocholic acid from the bile of haddocks, oxen, and dogs. Dogs' bile yields, in addition to the ordinary acid, a second crystalline taurocholic acid with a much more bitter taste. On hydrolysis with 8 per cent. sodium hydroxide at 100° , this acid yields a cholic acid melting at 182° . J. J. S.

The Stereochemistry of Chromium. I. PAUL PFEIFFER [and, in part, P. KOCH, G. LANDO, and A. TRIESCHMANN] (*Ber.*, 1904, 37, 4255—4290. Compare *Abstr.*, 1900, i, 559, 688; 1901, ii, 659; 1902, i, 138, 728; 1903, i, 464, 612).—The diacidodiethylenediaminechromium

salts, $[\text{En}_2\text{CrX}_2]\text{X}$ (where En = ethylenediamine), can exist in two stereoisomeric modifications, the *cis*- and *trans*-forms. The dithiocyanodiethylenediaminechromium salts described in Abstr., 1902, i, 138 are the *trans*-salts.

cis-Dithiocyanodiethylenediaminechromium thiocyanate, prepared by adding potassium thiocyanate to a solution of the *cis*-dichloro-chloride (violet salt), crystallises from warm water in orange scales or needles. No *trans*-salt is produced. A mixture of the two isomerides is obtained on warming potassium chromium thiocyanate with ethylenediamine or on warming the luteo-thiocyanate, $[\text{CrEn}_3](\text{SCN})_3$, with potassium thiocyanate, and may be separated by crystallisation from water.

cis-Dithiocyanodiethylenediaminechromium chloride,



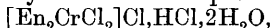
prepared by heating the thiocyanate with hydrochloric acid, forms glistening, ruby-red needles, and is less soluble in water than the *trans*-salt. The *cis*-bromide also contains H_2O , and forms ruby-red, prismatic needles; the *cis*-mercuri-iodide, $[\text{En}_2\text{Cr}(\text{SCN})_2]\text{I}, \text{HgI}_2$, is a fine, crystalline, orange precipitate. The *nitrate* forms small, reddish-orange needles. The *cis*-hydrogen sulphate forms star-shaped groups of orange needles containing $1\frac{1}{2}\text{H}_2\text{O}$.

Bromo-aquodiethylenediaminechromium bromide, $[\text{En}_2\text{Cr}(\text{OH}_2)\text{Br}]\text{Br}_2$, prepared by converting green chromium chloride hydrate into the pyridine compound (Abstr., 1902, i, 728), evaporating with ethylenediamine, and adding fuming hydrobromic acid, crystallises in red leaflets.

cis-Dichlorodiethylenediaminechromium chloride, $[\text{En}_2\text{CrCl}_2]\text{Cl}, \text{H}_2\text{O}$, may be prepared from the pyridine compound and hydrochloric acid, or by heating the luteo-chloride at 160° , or by passing a current of chlorine through an aqueous suspension of the dithiocyano-thiocyanate, and crystallises in reddish-violet needles, becoming anhydrous at 100° . Evaporation with concentrated hydrochloric acid and mercuric chloride partially converts it into the green *trans*-dichloro-chloride.

The *cis*-dichloro-bromide is precipitated by hydrobromic acid in small, violet needles containing H_2O and becoming anhydrous at 100° . The *iodide*, *nitrate*, *thiocyanate*, *dithionate*, and *hydrogen sulphate* form violet needles and are anhydrous; the *platinichloride* forms a violet precipitate and contains $12\text{H}_2\text{O}$.

trans-Dichlorodiethylenediaminechromium chloride, prepared by the action of chlorine on the *trans*-dithiocyano-thiocyanate, forms green or blue, strongly dichroic crystals of the composition



passing into the green, normal chloride at 100° . On evaporating with hydrochloric acid, after exposure to daylight, the violet *cis*-salt is obtained.

The *trans*-dichloro-bromide forms small, rhombic tablets, which are green by reflected, red by transmitted, light. The *iodide*, *thiocyanate*, and *nitrate* form greyish-green crystals, becoming pure green on heating, but recovering their original colour on cooling.

The configuration of the isomerides is determined by their relation to the oxalo-derivative. On warming the *cis*-dichloro-chloride with potassium oxalate, glistening, carmine-red crystals of a complex salt,

$[\text{En}_2\text{Cr}(\text{C}_2\text{O}_4)][\text{EnCr}(\text{C}_2\text{O}_4)_2] \cdot 1\frac{1}{2}\text{H}_2\text{O}$, are obtained, becoming anhydrous at 100° . Hydrobromic acid converts it into Werner and Schwarz's oxalobromide, $[\text{En}_2\text{Cr}(\text{C}_2\text{O}_4)]\text{Br}$. The *trans*-chloride, on similar treatment, yields a red, complex salt containing the unaltered *trans*-dichlorogroup, $[\text{En}_2\text{CrCl}_2]$. Hydrochloric acid converts the oxalodiethylenediaminechromium iodide into the *cis*-dichloro-iodide, no *trans*-compound being produced.

The stereochemical relations of the compounds described are summarised in tabular form, and a comparison is made between the complex chromium and cobalt salts. C. H. D.

Action of Acid Amides on Aldehydes. ALBERT REICH (*Monatsh.*, 1904, **25**, 933—942).—*iso*Butaldehyde and formamide, when heated together at 170 — 180° in presence of pyridine, form a small amount of *isobutylidenediformamide*, $\text{CHMe}_2\cdot\text{CH}(\text{NH}\cdot\text{COH})_2$, which crystallises in colourless needles, melts at 172° , decomposes when distilled under reduced pressure, is easily soluble in ether, less so in alcohol, and only slightly so in water, and is hydrolysed by dilute sulphuric acid, the product reducing ammoniacal silver solution and yielding ammonia when warmed with aqueous potassium hydroxide.

Propaldehyde and acetamide react at 170 — 180° in presence of pyridine to form *propylidenediacetamide*, $\text{CHEt}(\text{NHAc})_2$, which crystallises in small, silky needles, melts at 188° , decomposes when distilled, is easily soluble in alcohol, ether, or phenol, and, when boiled with dilute sulphuric acid, is hydrolysed to propaldehyde, ammonia, and acetic acid. G. Y.

Action of Acetamide on Aldehydes, and of Formamide on Acetophenone. MAX REICH (*Monatsh.*, 1904, **25**, 966—978. Compare preceding abstract).—When heated at 180° in presence of pyridine, *isobutaldehyde* and acetamide form *isobutylidenediacetamide*, $\text{CHPr}^i(\text{NHAc})_2$,

which crystallises in colourless needles, commences to sublime at 214° , melts and decomposes at 216° , is easily soluble in alcohol, ether, phenol, or bromoform, and is hydrolysed by boiling dilute sulphuric acid or 10 per cent. aqueous potassium hydroxide to *isobutaldehyde*, ammonia, and acetic acid.

Hexaldehyde and acetamide, in presence of pyridine at 180 — 185° , form *hexylidenediacetamide*, $\text{CH}_2\text{Pr}^a\cdot\text{CH}_2\cdot\text{CH}(\text{NHAc})_2$; it crystallises in leaflets, melts at 145° , is easily soluble in alcohol, ether, or phenol, and is hydrolysed by dilute sulphuric acid to hexaldehyde, ammonia, and acetic acid.

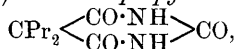
When heated with zinc chloride at 170 — 180° , acetophenone and formamide yield *s*-triphenylbenzene and a substance which crystallises in leaflets and small, slender needles, melts at 60° , has a slight, pleasant odour, does not evolve ammonia when treated by Kjeldahl's nitrogen method, and is probably a mixture of phenylpyrimidine (9 parts) and diphenylpyridine (2 parts). G. Y.

5:5-Dialkylbarbituric Acids and the Ureides of the Dialkylacetic Acids. EMIL FISCHER and ALFRED DILTHEY (*Annalen*, 1904, **335**, 334—368).—5:5-Diethylbarbituric acid (Conrad and Guthzeit,

Abstr., 1883, 314) is formed (yield, 70 per cent. of the theoretical) by the action of sodium ethoxide on ethyl diethylmalonate and carbamide in absolute alcoholic solution at 105—108°, or by the action of diethylmalonic chloride on carbamide. It crystallises from water in large, colourless, spear-like crystals, melts at 191° (corr.), sublimes slowly at 100°, is moderately soluble in hot water or alcohol, but only slightly so in ether, and has a bitter taste; it has a slightly acid reaction to litmus, and is easily soluble in aqueous alkali hydroxides, ammonia, calcium hydroxide, or baryta solutions. The *sodium* salt, $C_8H_{11}O_3N_2Na$, forms glistening crystals and is decomposed by carbon dioxide in aqueous solution.

5:5-Dimethylbarbituric acid is formed, in a yield of 39 per cent. of the theoretical, by the condensation of ethyl dimethylmalonate with carbamide in presence of sodium ethoxide. It crystallises from methyl alcohol in leaflets, melts at 279° (compare Thorne, Trans., 1881, 39, 545), and is more soluble in water than the diethyl acid. The *sodium* salt, $C_6H_6O_3N_2Na_2$, is obtained as a white, crystalline mass.

5-Methyl-5-ethylbarbituric acid, $CMeEt \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO}$, crystallises in long, flat needles and melts at 212° (corr.). 5-Methyl-5-propylbarbituric acid melts at 182° (corr.). 5:5-Dipropylbarbituric acid,



prepared by the condensation of ethyl dipropylmalonate and carbamide in presence of sodium ethoxide, or by the action of dipropylmalonic chloride on carbamide, crystallises in colourless plates and melts at 145° (corr.); the *sodium* salt, $C_{10}H_{15}O_3N_2Na$, crystallises in short prisms. 5-Ethyl-5-propylbarbituric acid crystallises in long, colourless, glistening needles and melts at 146° (corr.). 5:5-Diisobutylbarbituric acid crystallises in thin, colourless leaflets and melts at 173.5° (corr.). 5:5-Diisooamylbarbituric acid crystallises in slender, colourless needles and melts at 172° (corr.). 5:5-Dibenzylbarbituric acid crystallises in colourless plates and melts at 222° (corr.).

1-Methyl-5:5-diethylbarbituric acid, $CMe_2 \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO}$, obtained from ethyl diethylmalonate and methylcarbamide, forms colourless needles and melts at 154.5° (corr.). 1-Phenyl-5:5-diethylbarbituric acid, $CEt_2 \begin{smallmatrix} \text{CO} \cdot \text{NPh} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CO}$, crystallises in thin, colourless, glistening leaflets and melts at 197° (corr.). 1:3:5:5-Tetraethylbarbituric acid, $CEt_4 \begin{smallmatrix} \text{CO} \cdot \text{NEt} \\ \text{CO} \cdot \text{NEt} \end{smallmatrix} \text{CO}$, prepared by the action of diethylmalonic chloride on *s*-diethylcarbamide at 120—130°, is a colourless oil, boils at 125.5—126° (corr.) under 8.8 mm. pressure, has an ester odour, and is volatile with steam.

3-Thio-5:5-diethylbarbituric acid, $CEt_2 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CS}$, obtained by the condensation of ethyl diethylmalonate with thiocarbamide in presence of sodium ethoxide at 105°, crystallises in yellow needles, melts at 180° (corr.), and is moderately soluble in hot water, from which it crystallises in flat plates or prisms.

5 : 5-Diethylmalonylguanidine, $\text{CEt}_2\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\rangle\text{C}\cdot\text{NH}$, formed from ethyl diethylmalonate and guanidine in presence of sodium ethoxide, or by the action of diethylmalonic chloride or guanidine, crystallises in slender, colourless needles and decomposes without melting when heated. 5 : 5-Dipropylmalonylguanidine crystallises in white leaflets or plates, melts at 93° , and forms a crystalline *nitrate*; the *hydrochloride* crystallises in slender needles or thick prisms.

5-Methylbarbituric acid, $\text{CHMe}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$, obtained by the condensation of ethyl methylmalonate and carbamide in presence of sodium ethoxide, crystallises in microscopic plates or prisms, melts at $202\text{--}203^\circ$ (corr.), has an acid taste and reaction, and is easily soluble in boiling water, but only slightly so in alcohol; the *sodium salt*, $\text{C}_{10}\text{H}_{11}\text{O}_6\text{N}_4\text{Na}$, forms small, rose-coloured crystals, and, on addition of the calculated quantity of a mineral acid, yields the *neutral sodium salt*. 5-Ethylbarbituric acid is found to melt at 194° (corr.) (compare Conrad and Guthzeit, *loc. cit.*); when dissolved in aqueous sodium hydroxide and treated with ethyl iodide, it yields diethylbarbituric acid. 5-Propylbarbituric acid, $\text{CHPr}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$, melts at 208° (corr.); 5-isopropylbarbituric acid crystallises in long, thin plates and melts at 216° (corr.).

5-Bromo-5-methylbarbituric acid, $\text{CBrMe}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$, formed by shaking methylbarbituric acid with bromine water, forms colourless crystals, melts at $192\cdot5^\circ$ (corr.), and, when treated with alcoholic ammonia, yields 5-methyluramil, $\text{NH}_2\cdot\text{CMe}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$, which separates from water in colourless crystals, melts at 237° (corr.), and is more stable towards oxidising agents than is uramil. 5-Ethyluramil, $\text{NH}_2\cdot\text{CEt}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\rangle\text{CO}$, obtained from ethylbromobarbituric acid (Conrad and Guthzeit), melts and undergoes slight decomposition at 216° (corr.).

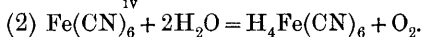
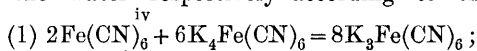
The ureides of dialkylmalonic acids are formed, sometimes along with the ureides of the corresponding dialkylacetic acids, by the action of fuming sulphuric acid on the mixture of dialkylmalonic acid and carbamide. Ureidodiethylmalonic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CO}_2\text{H}$, crystallises in thin, colourless leaflets, melts and decomposes at 162° (corr.), and has an acid taste and reaction. Ureidodipropylmalonic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CPr}_2\cdot\text{CO}_2\text{H}$, melts and decomposes at 147° yielding dipropylacetylcarbamide, which crystallises in slender needles and melts at $192\cdot5^\circ$.

The action of fuming sulphuric acid on a mixture of dimethylmalonic acid and carbamide leads to the formation of 5 : 5-dimethylbarbituric acid.

The ureides of dialkylacetic acids are also formed by the action of phosphorus oxychloride on a mixture of the acid and carbamide. α -Ethylbutyrylcarbamide, $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in colourless, slender needles, melts at $207\cdot5^\circ$ (corr.), is moderately soluble in

hot water, and is insoluble in dilute alkali hydroxides. When heated with hydrochloric acid of sp. gr. 1.19 in a sealed tube at 100°, it is hydrolysed with formation of α -ethylbutyric acid and carbamide. *α -Methylbutyrylcarbamide*, $\text{CHMeEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in colourless needles, melts at 178.5° (corr.), and is easily soluble in hot water. G. Y.

Influence of the Nature of the Anode on the Electrolytic Oxidation of Potassium Ferrocyanide. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1904, **139**, 855—857. Compare Abstr., 1903, ii, 352; 1904, ii, 229, 230, 414).—When a solution of potassium ferrocyanide is electrolysed in a vessel provided with a diaphragm, potassium ferricyanide and ferrocyanic acid are formed at the anode by the action of the anion, $\text{Fe}(\text{CN})_6^{\text{iv}}$, on the potassium ferrocyanide and the water respectively according to the equations:



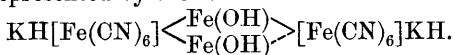
If, however, the anode is a metal capable of forming a ferrocyanide, the yield of the ferricyanide is diminished; and of the sixteen different metals examined in this respect, good yields of ferricyanide were obtained with such metals as platinum, which does not form a ferrocyanide, iron, which does not readily do so, and with copper, which is readily attacked, whilst magnesium, aluminium, and silver behaved like soluble anodes. The experiments were conducted in a nickel vessel which served as cathode, provided with a porous cell containing the anode; at the end of each experiment, the anode solution was measured, the unchanged ferrocyanide in a definite volume estimated by means of potassium permanganate in acid solution (Haen's method); in another quantity of the solution, the ferricyanide was reduced by means of hydrogen peroxide in alkali solution, and the total ferrocyanide estimated; the difference between the two results gave the amount of salt oxidised by electrolysis. M. A. W.

Blue Iron-cyanogen Compounds. KARL A. HOFMANN, O. HEINE, and F. HÖCHTLEN (*Annalen*, 1904, **337**, 1—36. Compare Abstr., 1900, i, 591).—In a detailed investigation of the properties and composition of the blue compounds obtained from ferrous and ferric salts and ferro- and ferri-cyanides, it is shown that the soluble Prussian blue prepared from potassium ferrocyanide (1 mol.) and a ferric salt (less than 1 mol.) is identical with soluble Turnbull's blue, prepared from potassium ferricyanide (1 mol.) and a ferrous salt (less than 1 mol.). Both are potassium ferric ferrocyanides, their composition corresponding very nearly with the formula $\text{Fe}(\text{CN})_6\text{KH}_2\text{Fe}(\text{OH})_2$ (compare Skraup, *Annalen*, 1877, **186**, 371).

The insoluble Prussian blue, which is obtained by addition of excess of a ferric salt or a mixture of a ferrous and a ferric salt to potassium ferrocyanide, is identical with the insoluble Turnbull's blue prepared by addition of excess of a ferrous salt to potassium ferri-

cyanide and washing the solid with full exposure to air. Both are ferric ferrocyanides, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 10\text{H}_2\text{O}$.

The insoluble greenish-yellow, crystalline solid remaining after the preparation of prussic acid is not identical with the precipitates obtained from ferrous salts and ferrocyanides. These precipitates are readily oxidised by the air to soluble or insoluble Prussian blue, whilst the residue is incompletely oxidised by the air, but oxidised by hydrogen peroxide to Williamson's violet. Although this violet has a composition identical with that of soluble Prussian blue, it differs from it in many respects, more especially in being more stable towards alkalis. It is suggested that it is a polymeride, and probably has the composition represented by the formula



In that case, the residue from the preparation of prussic acid has the constitution $\text{K}_2[\text{Fe}(\text{CN})_6] \left\langle \begin{smallmatrix} \text{Fe} \\ \text{Fe} \end{smallmatrix} \right\rangle [\text{Fe}(\text{CN})_6] \text{K}_2$, being the corresponding ferrous salt.

The blue compounds, Prussian blue, Turnbull's blue, and Williamson's violet, are all obtained when a mixture of ferricyanide and ferric salt is reduced by a reagent which will reduce the ferricyanide but not the ferric salt; such a reagent is hydrogen peroxide. In neutral or feebly acid solution, Prussian or Turnbull's blue is formed, whilst in strongly acid solution Williamson's violet is produced. These facts all demonstrate that in these substances ferric iron is combined with ferrocyanide and in no case ferricyanide with ferrous iron.

Attempts to prepare ferric ferrocyanide by the action of alcoholic ferric chloride on ferrocyanic acid led to the production of substances which contain both chlorine and alcohol. According to the proportions used and the conditions, temperature, &c., two or three different compounds were formed; they are dark blue powders and appear to be ferric ferrocyanides in which chlorine is still combined with the iron, and in which ethyl groups partly replace the hydrogen of the ferrocyanic acid.

K. J. P. O.

Electrolytic Preparation of Barium Platinocyanide. ANDRÉ BROCHET and JOSEPH PETIT (*Bull. Soc. chim.*, 1904, [iii], 31, 1265—1269. Compare Abstr., 1904, ii, 414).—A solution of barium cyanide, prepared by adding hydrocyanic acid to barium hydroxide suspended in water, is electrolysed in a vessel closed by a caoutchouc stopper provided with four holes, two of which carry the wires leading to the electrodes, the third a thermometer, and the fourth a funnel closed by glass wool to absorb splashes of liquid. The electrodes consist of sheet platinum suspended by thick platinum wire. The current employed is about 20 amperes, and the whole apparatus is placed in a bath of water so that the temperature of the electrolyte is between 50° and 60° and the operation is continued for about 8 hours. Carbon dioxide is then passed through the liquid and the precipitate filtered off, washed, and the filtrate and washings concentrated. On cooling, some barium platinocyanide crystallises out, and more may be procured by evaporating the mother liquor to dryness and extracting with methyl alcohol. The

platinocyanide may be obtained in small, green crystals by crystallisation from solutions of barium cyanide, and in this condition is markedly fluorescent. This form has the same composition as the ordinary platino-cyanide, $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, and not, as stated by Dammer, that represented by the formula $\text{Ba}_6\text{Pt}_5(\text{CN})_{22} \cdot 22\text{H}_2\text{O}$. T. A. H.

Theory of the Grignard Reaction and a New Method for the Preparation of Organo-magnesium Compounds. WLADIMIR TSCHELINZEFF (*Ber.*, 1904, 37, 4534—4540).—Grignard's organo-magnesium compounds may be prepared in the presence of benzene to which a small amount of ether or anisole has been added, or even in benzene or toluene solution alone if a sufficiently high temperature is employed (compare Brühl, *Abstr.*, 1903, i, 314; 1904, i, 139, 435; Malmgren, *Abstr.*, 1903, i, 710). The ether thus appears to be a catalytic agent, and the reaction is represented as occurring in the two stages: $\text{R}_2\text{O} + \text{R}'\text{X} = \text{R}_2\text{O} < \frac{\text{R}'}{\text{X}}$ and $\text{R}_2\text{O} < \frac{\text{R}'}{\text{X}} + \text{Mg} = \text{R} \cdot \text{Mg} \cdot \text{X} + \text{R}_2\text{O}$.

When only a small amount of ether, or when no ether, is used, the organo-magnesium compound separates as a solid without ether of crystallisation. It is also shown that a small amount of a tertiary amine, dimethylaniline, can be used in place of ether for the preparation of organo-magnesium compounds in the presence of benzene, hexane, turpentine, &c. The magnesium compound separates as a white, flocculent mass having the composition $\text{R} \cdot \text{Mg} \cdot \text{X}$. J. J. S.

Electrolytic Oxidation of the Hydrocarbons of the Benzene Series. I. Hydrocarbons containing the Methyl Group. H. D. LAW and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1904, 1, Reprint, 1—11).—When an emulsion of toluene with dilute acid or alkali is electrolysed, complete oxidation to carbon dioxide and water takes place. The electrolytic oxidation is best carried out by dissolving the hydrocarbon in acetone and stirring with 20 per cent. sulphuric acid in the anode cell, anodes of platinum gauze being employed. Lead cathodes in a solution of sulphuric acid or sodium sulphate are used. The current density is 1—2 amperes at the anode and the *E.M.F.* about 4 volts; the temperature must be kept low.

In each of the cases examined, the product is the aldehyde, a small quantity of a neutral compound, probably the corresponding alcohol, being formed at the same time. When several methyl groups are present, only one of them is oxidised to the aldehydic group. The addition of oxygen carriers has no influence on the result.

o-Tolualdehydesemicarbazone crystallises from amyl alcohol in small, white needles melting at 196° ; *p*-tolualdehydesemicarbazone forms small, white plates melting at 215° ; the phenylhydrazone is yellow, becoming red on exposure to light, and melts at 113° . The mixture of monoaldehydes obtained from ψ -cumene yields a semicarbazone, forming pearly-white plates and melting at 215.5° . 3:5-Dimethylbenzaldehyde, obtained from mesitylene, boils at 218 — 219° ; the semicarbazone forms pearly plates and melts at 201.5° . C. H. D.

Fluorobenzene and some of its Derivatives. [ARNOLD F. HOLLEMAN and] J. W. BEEKMAN (*Rec. Trav. Chim.*, 1904, **23**, 225—256).—Most of the results given in this paper have already appeared in *Abstr.*, 1904, i, 232 and 486. The present paper gives in addition details of the methods and apparatus employed and the yields of the various products obtained. T. A. H.

Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. X. Nitration of Dichlorobenzenes. ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1904, **23**, 357—379. Compare *Abstr.*, 1899, i, 759; 1900, i, 387, 638; 1901, i, 318, 591; 1902, i, 87; and 1903, i, 623).—The dichlorobenzenes were added drop by drop to nitric acid cooled to 0° or -30°. In the case of *o*-dichlorobenzene, the principal product in each case was 1:2-dichloro-4-nitrobenzene, and there was formed of the accessory product, 1:2-dichloro-3-nitrobenzene, 7.2 per cent. at 0° and 5.2 per cent. at -30°. With *m*-dichlorobenzene, the principal product was 1:3-dichloro-4-nitrobenzene, and the accessory product, 1:3-dichloro-2-nitrobenzene, was formed to the extent of 3.8 to 4.3 per cent. and 2.5 to 2.7 per cent. at 0° and -30° respectively. From the data available, it was considered unlikely that any 1:3-dichloro-5-nitrobenzene was formed in this reaction. The proportions of the respective isomerides formed were calculated by the methods already described (*loc. cit.*). The results obtained, taken in conjunction with those previously recorded (*loc. cit.*), show that the amount of accessory product formed increases with rise of temperature. In the nitration of dichlorobenzenes, the nitro-group takes up either the ortho- or para-position with regard to one chlorine atom, and the two positions which may be occupied are symmetrical with regard to the second atom of chlorine. The amount of accessory product formed during nitration is less in the case of the dichlorobenzenes and the halogenated benzoic acids (*Abstr.*, 1900, i, 387 and 591) than in the case of chlorobenzene; this is due to the influence of the second chlorine atom and of the carboxyl group in the two cases, and the effect is about twice as great when the perturbing group is in the *o*-position as when it occupies the *m*-position. 1:2-Dichloro-3-nitrobenzene, produced together with 1:4-chloro-3-nitrobenzene and hexachlorobenzene (?) by chlorinating *o*-chloronitrobenzene in presence of antimony chloride, is separated from its isomeride by fractional distillation and recrystallisation from acetic acid; it crystallises in silky needles and melts at 59.9°, boils at 257—258°, and has a sp. gr. 1.4494 at 79.5° (compare Beilstein and Kurbatoff, *Abstr.*, 1876, 632). 1:2-Dichloro-4-nitrobenzene melts at 43°, solidifies at 40.5°, boils at 255—256°, and has a sp. gr. 1.4514 at 80.18° (compare Beilstein and Kurbatoff, *Abstr.*, 1875, 450). 1:3-Dichloro-2-nitrobenzene, obtained from *p*-nitroaniline by the method described by Beilstein and Kurbatoff (*Abstr.*, 1879, 143), which was simplified in various ways, crystallises from alcohol and melts at 70°, solidifies at 70.05°, boils at 130° under 8 mm. pressure, and has a sp. gr. 1.4094 at 79.9°. 1:3-Dichloro-4-nitrobenzene (Beilstein and Kurbatoff, *Abstr.*, 1876, 632) melts at 31.5° to 32°, solidifies at 30.45°, boils at 258.5°, and has a sp. gr. 1.4390 at 79.7°. 1:3-Dichloro-5-nitrobenzene (*Abstr.*, 1875, 450),

prepared by chlorinating *p*-nitroaniline and diazotising the 2:6-dichloro-3-nitroaniline so produced, melts at 65°, solidifies at 63·15°, and has sp. gr. 1·4278 at 80·6°.

The specific gravities of the series of dinitroanisoles and dichloronitrobenzenes are tabulated in the original; the table shows that there is a fairly constant difference between the specific gravities of the ortho- and meta-isomerides in the two series. T. A. H.

Nitration of Disubstituted Benzenes. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 266—269. Compare Abstr., 1903, i, 623).—In the nitration of chlorobenzene at 0°, 29·8, 0·3, and 69·9 per cent. of *o*-, *m*-, and *p*-chloronitrobenzenes are respectively formed, whilst in the nitration of benzoic acid, 18·5, 80·2, and 1·3 per cent. of *o*-, *m*-, and *p*-nitrobenzoic acids are respectively formed. If the carboxyl and chlorine groups did not modify each other's directing influence, the nitro-derivatives obtained in the nitration of *o*-chlorobenzoic acid would be formed in the proportion represented by $(29·8 \times 80·2) : (69·9 \times 80·2)$, whilst in the nitration of *m*-chlorobenzoic acid the proportion would be represented by $(29·8 \times 18·5) : (69·9 \times 18·5)$; the proportions actually found in such cases were, however, 16:84 and 8·7:91·3 respectively.

Other similar cases are also quoted.

A. McK.

Action of Potassium Cyanide on ω -Nitrostyrolene [β -Nitrostyrene]. M. HOLLEMAN (*Rec. Trav. Chim.*, 1904, 23, 283—297).—When β -nitrostyrene, dissolved in alcohol, is treated with an aqueous solution of potassium cyanide and the mixture is acidified with acetic acid, there is precipitated the α -form of $\alpha\delta$ -dinitro- β -cyano- $\alpha\beta$ -diphenylbutane, $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CPh}(\text{CN}) \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{NO}_2$, whilst the β -isomeride of this remains dissolved and can be obtained by addition of excess of water. The α -form is colourless, crystallises from acetone on addition of light petroleum, and melts at 180° to 215° according to the rate of heating. The β -form crystallises from warm alcohol and melts and decomposes at 110·5°. Both forms, when heated with mineral acids in closed tubes, furnish diphenylsuccinic acid, hydroxylamine, and carbon dioxide and, when treated with alkalis, α -nitroacetophenone and hydrogen cyanide. Both isomerides reduce ammoniacal silver nitrate solution in the cold and the α -form is oxidised by potassium permanganate forming nitrous and benzoic acids. The formation of $\alpha\delta$ -dinitro- β -cyano- $\alpha\beta$ -diphenylbutane from β -nitrostyrene is explained in a manner analogous to that suggested by Poppe for the production of diethyl cyanodiphenylsuccinate by the action of potassium cyanide on ethyl α -bromophenylacetate (Abstr., 1890, 504). T. A. H.

Formation of 2-Acetyl-1:3-diketohydrindene by the Interaction of Phthalyl Chloride and Acetylacetone. CARL BÜLOW and MAX DESENISS (*Ber.*, 1904, 37, 4379—4382).—Sodioacetylacetone reacts in ethereal solution with phthalyl chloride forming *phthalylacetylacetone*, $\text{CO} < \text{C}_6\text{H}_4 > \text{C}:\text{C}(\text{CMe})_2$, which crystallises in colourless needles or rhombic plates melting at 129°. At the same time, owing to the

further action of the acid chloride on the acetylacetone, phthalyl-acetonylene is formed, which at once undergoes rearrangement into 2-acetyl-1:3-diketohydrindene melting at 110° . The presence of small quantities of phthalic acid, acetic acid, and acetylacetone in the ethereal solution was confirmed. E. F. A.

Action of Methylene Chloride and Aluminium Chloride on Toluene. JAMES LAVAUX (*Compt. rend.*, 1904, 139, 976—978).—The author finds that the compound melting at 232° obtained by Friedel and Craft by the action of methylene chloride and aluminium chloride on toluene (Abstr., 1887, 1102), and described as dimethylantracene, is a mixture of three isomeric dimethylantracenes melting at 240° , 244.5° , and 86° respectively, and of β -monomethylantracene. Anschütz's dimethylantracene, melting at 225° and obtained by the action of *s*-tetrabromoethane and aluminium chloride on toluene (Abstr., 1885, 768), is a similar mixture, but contains none of the isomeride melting at 86° . In addition to the anthracene derivatives already described, di-*m*- and di-*p*-tolylmethanes are also produced, together with benzene, xylene, and their homologues, by the action of methylene chloride and aluminium on the toluene, and the course of the reaction appears to be (1) the formation of the ditolylmethane derivatives by the direct action of toluene on the methylene chloride, (2) the interaction of this compound with a second molecule of methylene chloride to form a hydride of dimethylantracene, which reacts with a third molecule of the chloride to form methyl chloride and the corresponding anthracene derivative, (3) the xylene is formed by the interaction of the methyl chloride and toluene in the presence of aluminium chloride, (4) the benzene is formed from the toluene by the action of aluminium chloride, and, finally, (5) the β -monomethylantracene is the product of the reaction of benzene and toluene with methylene chloride. M. A. W.

Studies in the Phenanthrene Series. XVI. 9:10-Dichloro- and 9:10-Dibromo-phenanthrenes. A New Mode of Formation of *o*-Dichlorobenzene. JULIUS SCHMIDT and GUSTAV LADNER (*Ber.*, 1904, 37, 4402—4405. Compare Abstr., 1904, i, 1035).—9:10-Dichlorophenanthrene, prepared by heating 9-bromo-10-nitrophenanthrene with ammonium chloride for 6 hours at 320° , separates from alcohol in needles and melts at 160 — 161° . It may also be prepared by the action of chlorine on phenanthrene.

Similarly, *o*-chlorobenzene may be prepared by heating *o*-bromonitrobenzene with ammonium chloride for 12 hours at 320° . This method may possibly be a general one for the preparation of *o*-dichloro-substitution products of aromatic compounds.

9:10-Dibromophenanthrene, prepared in a similar manner from 9-bromo-10-nitrophenanthrene and ammonium bromide, separates from alcohol in needles and melts at 181 — 182° . A. McK.

Certain Tri-*p*-tolylmethane Derivatives. N. E. TOUSLEY and MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1904, 26, 1516—1523).—It has been shown by Gomberg and Voedisch (Abstr., 1901, i, 374) that by

the action of aluminium chloride on a mixture of carbon tetrachloride and toluene a tritolychloromethane is produced. A further investigation of this substance has proved it to be the tri-*p*-tolyl derivative.

Tri-*p*-tolylchloromethane crystallises from ethyl acetate or light petroleum, melts at 173°, and is readily soluble in benzene, ether, or carbon disulphide. A synthesis of the compound has been effected by the action of magnesium *p*-tolyl iodide on ethyl *p*-toluate.

Tri-*p*-tolylcarbinol, $C(C_6H_4Me)_3 \cdot OH$, prepared by heating the chloride with a mixture of sulphuric and acetic acids, forms large, colourless crystals, melts at 94°, and is soluble in ether, alcohol, benzene, or carbon disulphide, but only slightly so in light petroleum. An attempt was made to prepare hydroxyphenyltri-*p*-tolylmethane by the condensation of the carbinol with phenol (compare Baeyer and Villiger, Abstr., 1902, i, 769), but without success. The *ethyl* ether, obtained by the action of sodium ethoxide on tri-*p*-tolylchloromethane, crystallises in white, slender needles and melts at 111°. When tri-*p*-tolylcarbinol or its ethyl ether is treated with acetyl chloride, tri-*p*-tolylchloromethane is produced.

Tri-*p*-tolylbromomethane, $C(C_6H_4Me)_3Br$, obtained by the action of hydrogen bromide on tri-*p*-tolylcarbinol, forms yellow crystals and melts at 165°. When this compound is treated with bromine, a *perbromide*, probably a pentabromide, is produced, which forms orange-red crystals. A *periodide* was also obtained which crystallises in dark blue crystals with a metallic lustre and melts at 118–120°; this compound consists either of the tetra- or penta-iodide according to the conditions of the experiment.

When tri-*p*-tolylcarbinol is treated with hydrogen iodide, a *periodide* of tri-*p*-tolyliodomethane is formed, which melts at 138°. By the action of hydrogen iodide on a solution of tri-*p*-tolylcarbinol and iodine in carbon disulphide, the *penta-iodide* of tri-*p*-tolyliodomethane is produced, which forms dark, iridescent crystals and melts at 77°.

Tri-*p*-tolylmethane, $CH(C_6H_4Me)_3$, obtained by the reduction of tri-*p*-tolylchloromethane with zinc and acetic acid, distils at 260–262° under 28 mm. pressure.

When tri-*p*-tolylcarbinol is oxidised with chromic acid, the *acid*, $C(C_6H_4 \cdot CO_2H)_3 \cdot OH$, is produced, which, on heating, slowly volatilises without melting; its *lead*, *silver*, and *sodium* salts were prepared.

Tri-*p*-tolylaminomethane, $C(C_6H_4Me)_3 \cdot NH_2$, obtained by the action of ammonia on tri-*p*-tolylchloromethane, forms white crystals and melts at 112°.

Tri-*p*-tolylmethylaniline, $C(C_6H_4Me)_3 \cdot NHPh$, formed by the action of aniline on tri-*p*-tolylchloromethane, separates from acetone in white crystals, melts at 64°, and is soluble in ether, light petroleum, or toluene; when boiled with hydrochloric acid, it is converted into tri-*p*-tolylcarbinol, and, if heated with alcohol, tri-*p*-tolylcarbinol ethyl ether is produced. Tri-*p*-tolylmethyl-*p*-toluidine,

$C(C_6H_4Me)_3 \cdot NH \cdot C_6H_4Me$,
forms white crystals and melts at 151°.

The electrical conductivities of tri-*p*-tolylchloromethane and the corresponding bromo-derivative were determined at 20° in solution in benzonitrile. The results show that both compounds exhibit con-

siderable conductivity, that of the bromide being almost three times that of the chloride. When sulphur dioxide is used as the solvent, the molecular conductivity is much higher than when benzonitrile is employed. E. G.

Electrolysis of Acid Solutions of Aniline. LACHLAN GILCHRIST (*J. Physical Chem.*, 1904, **8**, 539—547).—Experiments were made to determine whether chloroaniline could be prepared by the electrolysis of hydrochloric acid solutions of aniline. No chloroaniline was obtained, however, aniline-black being apparently formed in each case. It was found that the decomposition voltage of aniline in either hydrochloric or sulphuric acid is about 0.95 volts, that is, lower than that of either of the acids; this is probably an oxidation potential and explains the non-formation of the chloro-derivative. As the value, however, is higher than the decomposition voltage of hydrobromic acid, it appeared probable that bromoaniline might be obtained electrolytically, and experiments showed that this was the case, crystals of bromoaniline, which melted at 116°, being obtained at the anode, whilst aniline-black was not produced. It was found that the oxidation potential of *m*-nitroaniline was 1.43 volts. L. M. J.

Formation of Protocatechuic Anilide. HUGO SCHIFF (*Bull. Soc. chim.*, 1904, [iii], **31**, 1220—1222).—It is asserted that Thibault's statement (*Abstr.*, 1904, i, 805) that Schiff's process of preparing this anilide yields an impure product is due to an inaccurate reading of the paper describing this method (*Abstr.*, 1883, 335). T. A. H.

Reactions of Ethyl Chlorosulphonate. O. W. WILLCOX (*Amer. Chem. J.*, 1904, **32**, 446—476).—It has been shown by Bushong (*Abstr.*, 1903, i, 732) that ethyl chlorosulphonate reacts with sodium alkyl oxides and with aniline as an alkylating agent. The alkylating action of this compound is regarded as being due to its dissociation according to the scheme $\text{Cl}\cdot\text{SO}_2\cdot\text{O}\cdot\text{CH}_2\text{Me} \rightleftharpoons \text{CHMe} + \text{Cl}\cdot\text{SO}_2\cdot\text{OH}$ (*Nef*, *Abstr.*, 1901, i, 626). The results of the present investigation indicate that a further change takes place involving the dissociation of a part of the chlorosulphonic acid into sulphur trioxide and hydrogen chloride.

When chlorosulphonic acid is added to a well cooled solution of dimethylaniline in chloroform, dimethylaniline hydrochloride and *dimethylanilinesulphurtrioxide*, $\text{NPhMe}_2\cdot\text{SO}_3$, are produced, the latter substance being obtained as a granular precipitate which, when heated to 60°, undergoes a transformation into dimethylaniline-*p*-sulphonic acid.

By the action of ethyl chlorosulphonate on dimethylaniline, ethyl chloride, phenyldimethylethylammonium chloride, and dimethylaniline-sulphurtrioxide are obtained. *Phenyldimethylethylammonium platini-chloride* crystallises in yellow needles.

Dimethylanilinesulphurtrioxide can also be prepared by the direct union of sulphur trioxide with dimethylaniline. It is decomposed readily by water with formation of dimethylaniline sulphate, $\text{NPhMe}_2\cdot\text{H}_2\text{SO}_4$, which melts at 84—85°, and when heated at 200° is

converted into dimethylaniline-*p*-sulphonic acid. Dimethylaniline-sulphurtrioxide combines with acetone with formation of an additive compound, $\text{NPhMe}_2 \cdot \text{SO}_3 \cdot \text{O} \cdot \text{CMe} \cdot \text{CH}_3$ or $\text{NPhMe}_2 \left\langle \begin{smallmatrix} \text{O} \\ \text{SO}_3 \end{smallmatrix} \right\rangle \text{CMe}_2$, which forms large prismatic crystals, melts at $76-78^\circ$, is soluble in water, and is decomposed by acids or alkalis with production of acetone, sulphuric acid, and dimethylaniline. An additive compound, obtained when dimethylanilinesulphurtrioxide is warmed with ethyl malonate, crystallises in white leaflets and is decomposed by aqueous alkali hydroxide with formation of ethyl malonate, sulphuric acid, and dimethylaniline. Dimethylanilinesulphurtrioxide reacts with phenol with formation of *phenyldimethylammonium phenyl sulphate*, $\text{NHMe}_2 \cdot \text{Ph} \cdot \text{SO}_3 \cdot \text{OPh}$, which is a crystalline substance, very soluble in water, and decomposed by aqueous potassium hydroxide into dimethylaniline and potassium phenyl sulphate. When aniline is brought into contact with dimethylaniline-sulphurtrioxide, combination takes place, and a wax-like substance, $\text{NHMe}_2 \cdot \text{Ph} \cdot \text{SO}_3 \cdot \text{NHPh}$, is produced, which is decomposed by barium hydroxide into dimethylaniline and barium phenylsulphamate. Trimethylethylene unites with dimethylanilinesulphurtrioxide with formation of an indistinctly crystalline substance, $\text{NMe}_2 \cdot \text{Ph} \left\langle \begin{smallmatrix} \text{CMe}_3 \\ \text{O} \cdot \text{SO}_3 \end{smallmatrix} \right\rangle \text{CHMe}$, which is decomposed by water into dimethylaniline, sulphuric acid, and trimethylethylene.

When a well cooled ethereal solution of diethylamine is treated with ethyl chlorosulphonate, triethylamine hydrochloride and tetraethylammonium chloride are produced together with *diethylsulphamic acid*, $\text{NEt}_2 \cdot \text{SO}_3 \text{H}$, which crystallises from benzene in colourless, orthorhombic prisms, melts at 89° , and is soluble in water, forming a solution with a strongly acid reaction. The *ethyl* ester, obtained by the action of sodium ethoxide on diethylsulphamic chloride (Behrend, Abstr., 1884, 285), is a colourless oil of a pleasant odour, which boils at 119° under 15 mm. and at 126° under 22 mm. pressure, but undergoes decomposition when heated under the ordinary atmospheric pressure; this compound does not react at the ordinary temperature with ammonia or diethylamine, and therefore cannot be formed as an intermediate product in the interaction of diethylamine and ethyl chlorosulphonate. Ethyl chlorosulphonate reacts with ammonia with formation of the hydrochlorides of diethylamine and triethylamine, tetraethylammonium chloride, and probably ammonium chloride and ammonium iminosulphonate, $\text{NH}(\text{SO}_3 \cdot \text{NH}_4)_2$, together with small quantities of ethyl ethylsulphamate and ethyl diethylsulphamate. When ethyl chlorosulphonate is added to aniline at the ordinary temperature, ethyl chloride and sulphanilic acid are produced (Wenghöffer, this Journal, 1877, ii, 147); if, however, the reaction is carried out at a low temperature, these substances are not produced, but ethylaniline is obtained together with sulphuric and phenylsulphamic acids, the two latter substances probably being produced by the hydrolysis of phenyliminodisulphonic acid, $\text{NPh}(\text{SO}_3 \text{H})_2$, formed as an intermediate product.

When ethyl chlorosulphonate is heated at 160° , it undergoes decomposition with formation of sulphur dioxide, sulphuric acid, ethylene,

hydrogen chloride, and a charred residue. If the compound is heated at 130° with powdered tin and a trace of iodine, ethylene, sulphur dioxide, stannic chloride, and small quantities of hydrogen chloride are produced.

In the following reactions, ethyl chlorosulphonate behaves not as an alkylating, but as a chlorinating agent. It reacts with ethyl sodio-acetoacetate with formation of ethyl α -chloroacetoacetate and small quantities of ethyl diacetylsuccinate. When ethyl sodiomalonate is similarly treated, ethyl acetylenetetracarboxylate is produced together with sodium ethyl sulphite and ethyl alcohol.

Ethyl hypochlorite also behaves as a chlorinating agent in its reaction with ethyl sodioacetoacetate and other compounds, such as sodium phenoxide, diethylamine, and trimethylethylene.

When ethyl chlorosulphonate is added to sodium phenoxide suspended in ether at 0° , sodium chloride, sodium sulphate, and phenetole are produced. E. G.

Ethylsulphone Derivatives of *p*-Phenetidine and their Pharmacological Importance. WILHELM AUTENRIETH and R. BERNHEIM (*Arch. Pharm.*, 1904, **242**, 579—589).—*Ethylsulphone-p-phenetidine*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\cdot\text{Et}$, was prepared from *p*-phenetidine (2 mols.) and ethylsulphonic chloride (1 mol.) in benzene solution; it melts at 80 — 81° and has the character of a monobasic acid. Its *acetyl* derivative melting at 78° and *benzoyl* derivative (obtained by heating it with benzoyl chloride at 130° , not by the Schotten-Baumann method) melting at 117° have no acid character. The *methyl* and *ethyl* derivatives melt at 49° and 57° respectively, and have no acid character. A *carbethoxy*-derivative was obtained by the action of alcoholic sodium ethoxide and ethyl chloroformate in succession; it melts at 112° and is poisonous. By nitration with dilute nitric acid (1 : 2) at the atmospheric temperature, or with gentle heat, *o-nitro-n-ethylsulphone-p-phenetide* [$\text{OEt}:\text{NO}_2:\text{N}$; &c., = 1 : 3 : 4] was obtained; it melts at 179° and is soluble in alkalis.

Ethyl p-phenetidine-N-carboxylate, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}_2\cdot\text{Et}$, was obtained from *p*-phenetidine (2 mols.) and ethyl chlorocarbonate (1 mol.) in benzene solution; it melts at $93\cdot5^{\circ}$; the hydrogen of its imino-group is not replaceable by metals or alkyl or acyl groups.

As was expected, to the antipyretic and antineuralgic properties conditioned by the *p*-phenetidine nucleus, *n*-ethylsulphone-*p*-phenetidine joins a certain sedative and hypnotic action due to the ethylsulphone group. Contrary to expectation, its carbethoxy-derivative, which contains yet another ethyl group, has no hypnotic action at all, instead of an increased one. C. F. B.

Iron Compounds of Salicylic Acid. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1904, **242**, 563—566).—When the violet liquid obtained by mixing aqueous solutions of ferric chloride and salicylic acid is shaken repeatedly with fresh quantities of ether or chloroform, the colour changes to red and finally disappears, whilst salicylic acid passes into the extract and colloidal ferric hydroxide remains in the aqueous solution. The violet colour is always obtained in the presence of a

certain amount of acid, the red colour when the acidity is small. It is suggested that these two colours correspond with two iron derivatives of salicylic acid, one of which may be derived from a ketonic form of the acid. C. F. B.

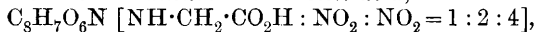
Reversion of some Secondary Cyclic Amines. PAUL LEMOULT (*Compt. rend.*, 1904, 139, 978—980).—Secondary amines of the type NHPhR , where R represents an alkyl group, undergo a reversion into aniline, the alkyl chloride RCl being evolved (compare Hess, *Abstr.*, 1885, 783; Auger, *Abstr.*, 1904, i, 805), when they are allowed to interact with phosphorus trichloride or pentachloride, and in the case of methylaniline the other products of the reaction are the same as those obtained in similar experiments with the phosphorus chlorides and aniline (compare *Abstr.*, 1903, i, 672; *Abstr.*, 1904, i, 380, 572); thus methylaniline yields, with phosphorus pentachloride, methylchloride, the hydrochloride of trianilinophenylphosphimide, and the anilide of phosphoric acid, and with phosphorus trichloride the same products together with hydrogen phosphide (compare *Abstr.*, 1904, ii, 728) and diphenylamine. M. A. W.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. II. HANS TH. BUCHERER (*J. pr. Chem.*, 1904, [ii], 70, 345—364. Compare *Abstr.*, 1904, i, 309).—The principal part of this paper consists of a discussion of the technical value of the reactions previously described (*loc. cit.*).

The formation of phenolic sulphites from mono- and di-alkylated aromatic amines takes place, in the same manner as from primary aromatic amines, on treatment with sodium hydrogen sulphite. The reverse reaction, the formation of secondary or tertiary amines by the action of a primary or secondary fatty amine and its sulphite on the phenol, or of the fatty amine on the phenolic sulphite, does not take place so easily as do the corresponding reactions with ammonia; thus, the reaction of α -naphthol-4-sulphonic acid with methylamine and methylamine sulphite, or of the sulphite of α -naphthol-4-sulphonic acid and methylamine, takes place at 125 — 150° , whilst these reactions with ammonia take place energetically at 90° .

The author proposes to use the series of reactions, $\text{R}\cdot\text{NHR}' \rightarrow \text{R}\cdot\text{O}\cdot\text{SO}_2\text{Na} (+ \text{NH}_2\text{R}') \rightarrow \text{R}\cdot\text{NH}_2 \rightarrow \text{R}\cdot\text{NHR}'$, where $\text{R}\cdot\text{NH}_2$ is α -naphthylamine-4-sulphonic acid and R' is an alkyl group, for the preparation of primary, and similarly through $\text{R}\cdot\text{NR}'\text{R}''$ for that of secondary fatty amines. G. Y.

Action of Bromodinitrobenzene on Glycine. ANDREA SANNA (*Gazzetta*, 1904, 34, ii, 221—224).—The action of 1-bromo-2:4-dinitrobenzene (1 mol.) on glycine (1 mol.) in pyridine solution yields pyridine hydrobromide and 2:4-dinitroanilinoacetic acid,



which crystallises from alcohol or water in shining, golden-yellow scales melting at 112° ; the acid is soluble in acetic acid and, to a slight extent, in benzene, light petroleum, or toluene. All its salts explode when heated rapidly. The silver salt, $\text{C}_5\text{H}_6\text{O}_6\text{N}_3\text{Ag}$, crystallises from

water or alcohol in rose-coloured needles which melt at 240° and are decomposed by boiling water; the *lead* salt crystallises from aqueous alcohol in minute, red needles melting at 173 — 174° ; the *barium* salt is yellow, very soluble in alcohol or water, and melts at 297° ; the calcium, mercuric, ferric, magnesium, cadmium, and zinc salts are obtained as red or yellow precipitates.

T. H. P.

Iodophenylcarbamides. RICHARD DOHT (*Monatsh.*, 1904, **25**, 943—965).—*p*-Iodophenylcarbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{I}$, is formed by the action of potassium cyanate on *p*-iodoaniline in glacial acetic acid solution or by the action of hydrochloric acid, potassium iodide, and potassium iodate on phenylcarbamide in boiling aqueous solution. It crystallises in monoclinic leaflets, melts irregularly, the same preparation being found to melt at 288° , 295° , and 300° , and, when boiled with acetic anhydride, yields *p*-iodoacetanilide and acetamide.

o-Iodophenylcarbamide, formed by the action of potassium cyanate on *o*-iodoaniline in glacial acetic acid solution, crystallises in needles, melts at 197 — 198° , is easily soluble in water, benzene, or acetone, and, when boiled with acetic anhydride, yields *o*-iodoacetanilide.

m-Iodophenylcarbamide, obtained from *m*-iodoaniline and potassium cyanate, crystallises in doubly refractive plates, melts at 174° , and, with acetic anhydride, yields *m*-iodoacetanilide.

The iodophenylcarbamides form acetyl derivatives when treated with acetyl chloride in pyridine solution. *Acetyl-p*-iodophenylcarbamide, $\text{NHAc} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{I}$, crystallises in doubly refractive plates, melts at 248° , and decomposes when heated above its melting point, and is hydrolysed by dilute sulphuric acid to *p*-iodoaniline, acetic acid, carbon dioxide, and ammonia. *Acetyl-o*-iodophenylcarbamide crystallises in monoclinic prisms and melts at 182° . *Acetyl-m*-iodophenylcarbamide crystallises in monoclinic plates or rhombic prisms and melts at 201° .

When heated with aniline, the iodophenylcarbamides yield *s*-diphenyl carbamide, ammonia, and the corresponding iodoaniline.

G. Y.

Persubstituted Dithiobiurets. OTTO C. BILLETER and HENRI RIVIER [and, in part, AL. MARET] (*Ber.*, 1904, **37**, 4317—4326. Compare Abstr., 1893, i, 575; Freund, Abstr., 1895, i, 576; Johnson, Abstr., 1903, i, 751).—Persubstituted normal dithiobiurets, containing an aryl group attached to the central nitrogen atom ("mesoaromatic"), undergo rearrangement with hydrogen chloride in chloroform solution, yielding the hydrochlorides of the isomeric ψ -dithiobiurets. In the case of unsymmetrical compounds, a mixture of the two isomeric ψ -compounds is obtained if the substituted amino-groups differ but little from one another (as NPhMe and NPhEt), but when the difference is considerable (as NMe_2 and NPhEt), only one compound is obtained. When an alkyl group is attached to the central nitrogen atom ("mesoaliphatic"), hydrogen chloride does not cause rearrangement, but the molecule is completely broken down.

Of the isomeric ψ -dithiobiurets, that compound is designated by α in which the amine residue of lower molecular weight is attached to the thiocarbonyl, the other isomeride being β .

Symmetrical.—*ac-Diphenyldimethyl-1-phenyl-ψ-dithiobiuret*,
 $\text{NPhMe} \cdot \text{CS} \cdot \text{S} \cdot \text{C}(\text{NPh}) \cdot \text{NPhMe}$,

forms pale yellow tablets melting at 139° , but is converted on slowly heating into the normal compound, $\text{NPhMe} \cdot \text{CS} \cdot \text{NPh} \cdot \text{CS} \cdot \text{NPhMe}$, which forms yellow needles melting at 203° . *ac-Diphenyldiethyl-1-phenyl-ψ-dithiobiuret* melts at 120° and the normal compound at 158.5° . *ac-Diphenyldipropyl-1-phenyl-ψ-dithiobiuret* forms a crystalline powder melting at $85.5\text{--}86^\circ$; it slowly passes in alcoholic solution into the sparingly soluble normal compound melting at $158\text{--}158.5^\circ$.

ac-Diphenyldiethyl-1-α-naphthyl-ψ-dithiobiuret forms pale yellow prisms melting at $113.5\text{--}114^\circ$, and is converted on boiling its alcoholic solution into the normal compound melting at $158\text{--}158.5^\circ$. The *β-naphthyl-ψ*-compound melts at $127.5\text{--}128^\circ$, and the normal compound at $130\text{--}130.5^\circ$.

Unsymmetrical.—*α-Diphenylmethylethyl-1-phenyl-ψ-dithiobiuret* forms yellow needles melting at $118\text{--}119^\circ$; the *β*-compound is a crystalline powder melting at $136\text{--}136.5^\circ$; the *n*-compound melts at $158.5\text{--}159^\circ$. *α-Diphenylmethylpropyl-1-phenyl-ψ-dithiobiuret* forms silky scales melting at $122.5\text{--}123^\circ$; the *β*-compound forms pale yellow prisms and melts at $119.5\text{--}120^\circ$; the *n*-compound melts at $125.5\text{--}126^\circ$ (compare Billeter and Strohl, Abstr., 1888, 364). *α-Diphenylethylpropyl-1-phenyl-ψ-dithiobiuret* forms bright yellow leaflets melting at $89.5\text{--}90^\circ$; the *β*-compound melts at $76\text{--}76.4^\circ$ and the *n*-compound at 165.8° . *α-Phenyl-dimethyl-1-phenyl-ψ-dithiobiuret* forms colourless needles melting at $91.6\text{--}92^\circ$; the *β*-compound forms yellow needles and melts at 95° ; the *n*-compound melts at 98.8° . *α-Dimethyldipropyl-1-phenyl-ψ-dithiobiuret* melts at $64.6\text{--}65^\circ$, the *β*-compound at $48.6\text{--}48.8^\circ$, and the *n*-compound at $80.5\text{--}81^\circ$.

Diphenyldiethyl-1-ethyl-ψ-dithiobiuret melts at 82.6° and the *n*-compound at 158.8° . Hydrogen chloride decomposes it, ethylaniline and ethylthiocarbimide being recognised among the products. *Diphenyldiethyl-1-allyl-ψ-dithiobiuret*, from allylphenylethylthiocarbimide and phenylethylthiocarbamide chloride, melts at 58.5° ; the *n*-compound melts at $143.4\text{--}143.6^\circ$.

Diphenyldimethyl-1-benzyl-ψ-dithiobiuret is uncrystallisable; the *n*-compound forms yellow leaflets and melts at $124.8\text{--}125^\circ$. The *n-diethyl* compound melts at $129.5\text{--}130^\circ$.

α-Phenyldimethylethyl-1-ethyl-ψ-dithiobiuret forms colourless prisms melting at $66.5\text{--}67^\circ$; the *β*-compound forms pale yellow, rhombic tablets and melts at $42.8\text{--}43^\circ$; the *n*-compound forms colourless prisms and melts at $113.5\text{--}114^\circ$, and is decomposed by hydrogen chloride in chloroform solution, forming ethylaniline, ethylthiocarbimide, and *dimethylxanthogenamide*, melting at 13.8° and boiling at 82.6° under 10 mm. pressure. The latter compound is a secondary product, derived from the action of alcohol on the dimethylthiocarbamide chloride first produced.

β-Diphenylethyl-1-phenyl-ψ-dithiobiuret, $\text{NPhEt} \cdot \text{CS} \cdot \text{S} \cdot \text{C}(\text{NPh}) \cdot \text{NHPh}$, forms yellow needles melting at 91° and decomposing to form carbon disulphide and triphenylethylguanidine.

Phenyl-α-naphthylmethylthiocarbamide, $\text{NPhMe} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$, forms

colourless crystals melting at 135·5—136°. The β -naphthyl compound is colourless and melts at 124·5—125° (compare Gebhardt, Abstr., 1884, 1320).

Phenyl- α -naphthylethylthiocarbamide forms colourless tablets and melts at 129—129·5°, and the β -naphthyl derivative at 128·5—129°.

C. H. D.

Mononitro-derivatives of *p*-Aminophenol. FRÉDÉRIC REVERDIN and AUGUSTE DRESEL (*Ber.*, 1904, **37**, 4452—4456; *Bull. Soc. chim.*, 1904, [iii], **31**, 1269—1273).—When the directions given by Hübner, Morse, and Gussefeldt (Abstr., 1882, 505) for the preparation of benzoyl-*p*-aminophenol are followed, *p*-benzoylamino-phenyl benzoate is produced, which melts at 233—234°, and on nitration with nitric acid of sp. gr. 1·52, the temperature not being allowed to rise beyond 25°, furnishes a *dinitro-p-benzoylamino-phenyl benzoate*, which melts at 229° and on saponification yields *dinitro-p-aminophenol*: the latter crystallises from water or benzene in red needles with a green sheen and melts at 230—231°; the *acetyl* derivative forms yellow needles and melts at 182°. If nitric acid of sp. gr. 1·48 is employed for the nitration at temperatures from 0° to 10°, there is formed 3-*nitro-4-benzoylamino-phenyl benzoate*, which exists in two modifications: one form consisting of yellow needles, the other of hard, brown crystals, and both melting at 147°. On saponification with sulphuric acid, this yields 3-nitro-4-aminophenol (m. p. 154°). These results prove that the benzoyl-*p*-aminophenol (m. p. 227·5°), the *m*-nitrobenzoyl-*p*-aminonitrophenol (m. p. 228°), and the *p*-aminonitrophenol (m. p. 183°) described by Hübner (*loc. cit.*) do not exist.

Nitro-derivatives of the aminophenols are best obtained by nitrating products in which the amino- and hydroxyl-groups are both protected, for example, *p*-acetylamino-phenyl acetate.

3-Nitro-4-acetylamino-phenyl acetate, when treated in the cold with a 40 per cent. solution of sodium hydroxide in water or with sulphuric acid, yields 3-*nitro-4-acetylamino-phenol*, which crystallises from water in brownish-yellow needles and melts at 218°. *p*-Tolylsulphone-phenyl-oxamide *p*-tolylsulphonate crystallises from benzene in white needles and melts at 169°; the *acetyl* derivative forms yellow, prismatic needles and melts at 150—152°, and the *m*-nitro-derivative, obtained by nitration with nitric acid of sp. gr. 1·48 at 10—15°, yellowish-brown prisms melting at 139°, and on saponification yields *m*-nitro-*p*-aminophenol.

T. A. H.

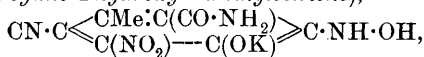
Constitution of Aromatic Purpuric Acids. VI. The Purpurate Reaction with 2:6-Dinitrophenols. WALTHER BORSCHKE and E. BÖCKER (*Ber.*, 1904, **37**, 4388—4397. Compare Abstr., 1904, i, 574).—Whilst picric acid behaves like 2:4-dinitrophenols with respect to purpurate formation, one hydrogen atom being replaced by the cyanogen group and the nitro-group replaced by a NH·OH group, the behaviour of 3:5-dinitro-*p*-cresol and of ethyl 3:5-dinitro-4-hydroxybenzoate is different, since the resulting purpuric

acids contain $1\text{H}_2\text{O}$ more than was expected. In the latter cases, it is supposed that one of the cyanogen groups introduced is hydrolysed to the $\text{CO}\cdot\text{NH}_2$ group.

By variation of the experimental conditions, it is possible to obtain, from picric acid, a salt of the acid $\text{C}_8\text{H}_5\text{O}_7\text{N}_5$, containing $1\text{H}_2\text{O}$ more than the *isopurpurate*; further, the normal purpurate, $\text{C}_{11}\text{H}_7\text{O}_8\text{N}_4\text{K}$, may be obtained from potassium cyanide and ethyl 3:5-dinitro-4-hydroxybenzoate.

In the 2:6-dinitrophenol purpurates, the two cyanogen groups do not unite with water with the same ease. In purpurate formation, hydrogen cyanide, and not potassium cyanide, is added on, and the cyanogen groups are not introduced successively, but simultaneously.

Potassium p-cresolpurpurate (*potassium-3-nitro-5-hydroxylamino-6-carboxylamido-2-cyano-4-hydroxy-1-methylbenzene*),

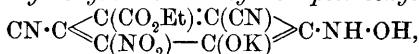


prepared by warming an alcoholic solution of 3:5-dinitro-*p*-cresol with an aqueous solution of potassium cyanide, forms a brown, crystalline powder.

Ammonium-p-cresolpurpurate, prepared by decomposing potassium *p*-cresolpurpurate by phosphoric acid and then adding an ethereal solution of ammonia to the ethereal solution of the liberated *p*-cresolpurpuric acid, is a brown, unstable powder. The free acid is a dark brown powder which explodes on being heated.

When potassium *p*-cresolpurpurate is heated with aqueous potassium hydroxide, it forms *methyl nitrohydroxylaminopotassoxisophthalamate monoamide*, $\text{C}_9\text{H}_9\text{O}_8\text{N}_3\text{K}_2$, which crystallises in needles and, when acted on by phosphoric acid, forms *methyl hydroxylaminonitrohydroxysophthalic monoamide*, separating in bluish-black crystals.

Ethyl 3-nitro-5-hydroxylamino-2:6-cyano-4-potassoxybenzoate,



prepared from ethyl 3:5-dinitro-4-hydroxybenzoate and potassium cyanide when the compound, $\text{C}_9\text{H}_7\text{O}_7\text{N}_2\text{K}\cdot 2\text{HCN}$, first formed undergoes transformation in a manner not exactly determined, is a "normal" purpurate and is bluish-green.

Ethyl 3-nitro-5-hydroxylamino-6-carboxylamido-2-cyano-4-potassoxybenzoate, $\text{CN}\cdot\text{C}\begin{array}{c} \text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}\cdot\text{NH}_2) \\ \text{C}(\text{NO}_2)\text{---C}(\text{OK}) \end{array}\text{C}\cdot\text{NH}\cdot\text{OH}$, prepared by the action of ethyl 3:5-dinitro-4-hydroxybenzoate on potassium cyanide at a higher temperature than in the preceding case, separates from water in brick-red needles. The corresponding *ammonium* salt has similar physical properties.

Potassium isopurpurate (*1:3-dinitro-5-hydroxylamino-2:6-cyano-4-potassoxybenzene*), $\text{CN}\cdot\text{C}\begin{array}{c} \text{C}(\text{NO}_2)\cdot\text{C}(\text{CN}) \\ \text{C}(\text{NO}_2)\cdot\text{C}(\text{OK}) \end{array}\text{C}\cdot\text{NH}\cdot\text{OH}$, prepared from picric acid and potassium cyanide, forms a dark red mass, as also does the *ammonium* salt. The free acid is dark violet.

1:3-Dinitro-5-hydroxylamino-6-carboxylamido-2-cyano-4-potassoxybenzene, prepared from picric acid and potassium cyanide at $50\text{--}60^\circ$, is a dark coloured, explosive compound.

A. McK.

Symmetrical Trinitroxyleneol. EDMUND KNECHT (*Ber.*, 1904, **37**, 4193).—*s*-Trinitroxyleneol (Knecht and Hibbert, *Abstr.*, 1904, **i**, 871) has been previously described by Blanksma (*Abstr.*, 1902, **i**, 286).

C. H. D.

Occurrence of a Dihydrocuminol in Ginger Grass Oil. HEINRICH WALBAUM and O. HÜTHIG (*Chem. Zeit.*, 1904, **28**, 1143).—The dihydrocuminol, $C_{10}H_{16}O$, obtained from Ginger grass oil, boils at 228—229° under 755 mm. and at 94·5—96° under 4—5 mm. pressure; it has the sp. gr. 0·9536 at 15°, $\alpha_D + 12^\circ 5'$ (length of tube not stated), and n_D 1·49761 at 20°. When oxidised by chromic acid, it forms the aldehyde, $C_{10}H_{14}O$, which, when oxidised by silver oxide, forms the acid, $C_{10}H_{14}O_2$, which is probably dihydrocuminic acid. When the latter acid is oxidised by dilute nitric acid, it forms cuminic acid, whilst concentrated nitric acid converts it into 3-nitrocuminic acid.

When the dihydrocuminol is warmed with a concentrated solution of formic acid, cymene is formed.

A. McK.

Geometrical Isomerism of Derivatives of Diphenylethylene.

RICHARD STOERMER and M. SIMON (*Ber.*, 1904, **37**, 4163—4168).—Geometrical isomerism is possible in derivatives of diphenylethylene when one hydrogen atom of the methylene group and one atom in a benzene nucleus are replaced. In the following, the compound with the higher melting point, which is also the less soluble, is designated the α -, the other the β -isomeride. The actual configuration has not been determined.

Phenyl-*o*-anisylbromoethylene, $CHBr:CPh \cdot C_6H_4 \cdot OMe$ (O. Kippe, *Diss. Rostock*, 1904), may be separated into two fractions by crystallisation from alcohol. The α -compound forms long needles melting at 78·5°; the β -compound forms indefinite crystals and melts at 56·5°. Sunlight slowly converts the alcoholic or ethereal solution of the α - into the β -compound, but the transition could not be effected by any other means.

Phenyl-*o*-anisylchloroethylene, prepared by passing chlorine into a solution of phenyl-*o*-anisylethylene in carbon disulphide, forms small, highly refractive cubes and melts at 90°. On heating under reduced pressure or with alcoholic sodium hydroxide, the *monochloro*-compound is obtained and may be separated by crystallisation. The α -compound forms long, glistening prisms and melts at 71·5°; the β -compound forms short crystals melting at 50·5°. Sunlight converts the α - into the β -form.

Phenyl *p*-anisylethylene, prepared from phenyl-*p*-anisyl ketone and magnesium methyl iodide, forms silvery leaflets and melts at 75°. The α -bromo-derivative melts at 82·5° and the β -derivative at 52°.

α -Phenyl-*p*-anisylchloroethylene melts at 59—60° and the β -compound at 26—28°.

α -Phenyl- α -naphthylbromoethylene melts at 71—72° and the β -compound at 54°.

p-Bromodiphenylethylene, prepared from *p*-bromobenzophenone and

magnesium methyl bromide, boils at 199—201° under 19 mm. pressure. *a-p-Bromodiphenylbromoethylene* forms glistening prisms and melts at 107°; the β -compound melts at 35°. C. H. D.

Conversion of Nitronaphthalenes into Nitroso-derivatives of Naphthol. CARL GRAEBE (*Annalen*, 1904, **335**, 139—144. Compare Abstr., 1900, i, 24; Friedländer, Abstr., 1900, i, 150).—1:6-Dinitro- β -naphthyl methyl ether, $C_{11}H_8O_5N_2$, is best prepared by the action of methyl sulphate on the potassium compound; it crystallises in brown needles, melts at 202°, and yields 1:6-dinitro- β -naphthylamine when heated at 155—160° with alcoholic ammonia.

When treated with sulphuric acid containing 15—17 per cent. of anhydride at 40—50°, 1:6-dinitronaphthalene yields a *nitronitroso-naphthol*, which crystallises in brown needles, decomposes above 200°, dissolves in concentrated sulphuric acid to a yellow, in aqueous alkali hydroxides to reddish-brown solutions, yields 4-nitrophthalic acid when oxidised with potassium permanganate, and is probably 7-nitro-4-nitroso- α -naphthol.

When treated with fuming sulphuric acid, 1:3-dinitronaphthalene yields a *product* which is insoluble in water, but easily soluble in aqueous alkali hydroxides. G. Y.

5:4- and 8:4-Nitronitroso- α -naphthols. CARL GRAEBE and A. OESER (*Annalen*, 1904, **335**, 145—156. Compare foregoing abstract).—5-Nitro-4-nitroso- α -naphthol (Abstr., 1900, i, 24, 150) crystallises in yellow needles, decomposes at 250—260°, is insoluble in water, but easily soluble in alcohol, glacial acetic acid, or aqueous alkali hydroxides, and dissolves in concentrated sulphuric acid to a yellow solution; a yellow, crystalline precipitate is formed on addition of lead acetate to a solution of the nitrosonitronaphthol in aqueous ammonia. With dilute nitric acid at the ordinary temperature, it is oxidised to naphthapicric acid; with alkaline potassium permanganate, to 3-nitrophthalic acid.

8-Aminonaphthaquinol (8-amino-1:4-dihydroxynaphthalene) hydrochloride, obtained by reduction of 5-nitro-4-nitroso- α -naphthol with tin and hydrochloric acid, crystallises in colourless needles and gives a red, crystalline *precipitate* when treated with ferric chloride.

8-Acetyl-amino-1:4-naphthaquinone, obtained by oxidation of 8-acetylaminonaphthaquinol, crystallises in leaflets and melts at 162°.

4:5-Diamino- α -naphthol hydrochloride is obtained by reduction of 5-nitro-4-nitroso- α -naphthol with stannous chloride at the ordinary temperature.

8-Nitro-4-nitroso- α -naphthol, obtained from 1:5-dinitronaphthalene, forms yellow crystals and decomposes at 235—240°; the *barium* derivative, $(C_{10}H_5O_4N_2)_2Ba \cdot 3H_2O$, forms yellow crystals.

4:8-Dinitro- α -naphthol melts at 235° (compare Abstr., 1900, i, 150); the *potassium* and *ammonium* derivatives are easily soluble in boiling water; the *silver* derivative is red; the *ethyl* ether crystallises in brown needles and melts at 115°. G. Y.

Action of Bromine and Chlorine on Phenols : Substitution Products ; ψ -Bromides and ψ -Chlorides. XII. ψ -Bromo-*p*-dihydroxystilbene, Stilbenequinone, and their Products. THEODOR ZINCKE and S. MÜNCH (*Annalen*, 1904, 335, 157—191. Compare Abstr., 1902, i, 178, 179).—*Di-p-hydroxystilbene ψ -dibromide*,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ or $\text{C}_6\text{H}_5\text{O}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{C}_6\text{H}_5\text{O}$, is obtained by the action of bromine on di-*p*-hydroxystilbene in ethereal solution cooled by a freezing mixture. It crystallises in small leaflets, or from acetone in needles, decomposes when heated, loses bromine with regeneration of dihydroxystilbene on prolonged boiling in acetone, gives an intense red coloration and separation of a green substance when treated with aqueous sodium hydroxide, and yields stilbenequinone when acted on by water or sodium carbonate solution.

Stilbenequinone, $\text{C}_6\text{H}_4\text{O}:\text{CH}:\text{CH}:\text{C}_6\text{H}_4\text{O}$, is prepared by shaking an ethereal suspension of the ψ -dibromide with aqueous sodium acetate. It crystallises in small, red needles, is unstable when moist, reacts easily with alcohol, acetic acid, and acetic anhydride, and is reduced by stannous chloride to di-*p*-hydroxystilbene.

In contact with acetone, stilbenequinone yields a white polymericide (?) which, with concentrated sulphuric acid, regenerates the quinone.

Di-p-hydroxystilbene- ψ -dichloride, formed by the action of hydrogen chloride on stilbenequinone in glacial acetic acid solution, crystallises in thick needles and resembles the ψ -dibromide.

Stilbenequinhydrone, $\text{O} < \text{C}_6\text{H}_4 \text{---} \text{CH}:\text{CH} \text{---} \text{C}_6\text{H}_4 > \text{O}$, formed by the action of stilbenequinone on di-*p*-hydroxystilbene, by the action of the ψ -dibromide on di-*p*-hydroxystilbene in presence of sodium acetate, or by oxidation of di-*p*-hydroxystilbene with ferric chloride, crystallises in small, green needles which are violet by transmitted light, is sparingly soluble, and is converted into di-*p*-hydroxystilbene on prolonged treatment with water.

The green *sodium* derivative of stilbenequinhydrone is formed by the action of bromine water on an alkaline solution of di-*p*-hydroxystilbene or by the action of aqueous sodium hydroxide on stilbenequinone or the ψ -dibromide.

The action of methyl alcohol on the ψ -dibromide leads to the formation of three dimethoxy-derivatives.

The *quinone*, $\text{C}_2\text{H}_2(\text{OMe})_2 \left(\text{CH} < \text{CH}:\text{CH} > \text{CO} \right)_2$, formed by the action of methyl alcohol on the ψ -dibromide in ethereal solution, crystallises in small, colourless needles, yields stilbenequinone when dried over sulphuric acid, and is easily soluble in aqueous alkali hydroxides.

Di-p-hydroxyhydrobenzoin dimethyl ether, $\text{C}_2\text{H}_2(\text{OMe})_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$, obtained on the addition of an acid to the alkaline solution of the quinone form, crystallises in large plates and melts and decomposes at 220° ; the *diacetyl* derivative crystallises in short prisms and melts at 153° .

Di-p-hydroxyisohydrobenzoin, formed along with the hydrobenzoin derivative by the action of methyl-alcoholic potassium hydroxide on the ψ -dibromide, crystallises in thick needles and melts at 205° the

diacetyl derivative crystallises in colourless needles, melts at 91° , and is more soluble in benzene than the isomeride.

Di-p-acetoxystilbene dibromide, $C_2H_2Br_2(C_6H_4 \cdot OAc)_2$, obtained by the action of bromine on di-*p*-acetoxystilbene, by acetylation of the ψ -dibromide with acetic anhydride, and by addition of acetyl bromide to stilbenequinone, occurs in two forms. The hydrobenzoin form crystallises in colourless needles, melts, with evolution of hydrogen bromide, at 215° , slowly decomposes at the ordinary temperature, and when treated with concentrated sulphuric acid yields acetyl bromide and stilbenequinone. The *isohydrobenzoin* derivative crystallises in thick needles, melts at 170° , and is more soluble than its isomeride. If heated carefully to its melting point, the *isohydrobenzoin* compound undergoes isomeric change into the higher melting modification.

Di-p-acetoxystilbene dichloride is obtained in two modifications: the one crystallises in long, colourless needles and melts and decomposes at 220° ; the other crystallises from methyl alcohol in needles, from benzene in prisms containing benzene of crystallisation, melts at 132° , and is converted into the higher melting modification when heated with glacial acetic acid and hydrogen chloride at 100° , or when heated above its melting point until evolution of hydrogen chloride commences. When treated with methyl alcoholic potassium hydroxide, both dichlorides yield the dimethyl ether of dihydroxyhydrobenzoin and di-*p*-hydroxytolane. With alkali hydroxides in acetone solution, the dichlorides yield dihydroxystilbene.

Di-p-acetoxylbromostilbene, $OAc \cdot C_6H_4 \cdot CH : CBr \cdot C_6H_4 \cdot OAc$, obtained by heating di-*p*-acetoxystilbene dibromide (m. p. 215°) until completely melted, crystallises in colourless needles, melts at 126 – 127° , and yields di-*p*-hydroxytolane when treated with alcoholic potassium hydroxide. *Di-p-acetoxylchlorostilbene* crystallises in long leaflets and melts at 125 – 126° to an opaque, doubly-refracting liquid, which becomes clear at 138° .

Di-p-hydroxytolane, $OH \cdot C_6H_4 \cdot C : C \cdot C_6H_4 \cdot OH$, crystallises in needles and melts at 220 – 225° ; the *diacetyl* derivative crystallises in long needles and melts at 198° . When treated with concentrated sulphuric acid, dihydroxytolane and its *diacetyl* derivative yield an intensely red, crystalline *substance* of a quinonoid nature, which dissolves in glacial acetic acid to a red, in aqueous alkali hydroxides to a violet, solution.

The action of acetic anhydride and sodium acetate on di-*p*-acetoxyhydrobenzoin dibromide leads to the formation of (1) the *tetra-acetyl* compound, $C_2H_2(OAc)_2(C_6H_4 \cdot OAc)_2$, which is obtained in two modifications, the one crystallising in thick needles, containing benzene of crystallisation, and melting at 172 – 173° ; the other crystallising in slender needles and melting at 124 – 125° ; and (2) *dihydroxystilbene diacetate*, which crystallises in needles and melts at 211 – 212° . G. Y.

Mixed Phenolic Sulphides. F. TABOURY (*Bull. Soc. chim.*, 1904, [iii], 31, 1183–1188. Compare *Abstr.*, 1903, i, 748).—When an alkyl haloid reacts with the compounds obtained by the interaction of sulphur with magnesium alkyl haloids (*loc. cit.*), mixed sulphides are produced. *Phenyl benzyl sulphide*, $CH_2Ph \cdot S \cdot Ph$, crystallises in white

lamellæ and melts at 40—41°; its solution in sulphuric acid becomes orange on warming. *p*-Bromophenyl methyl sulphide melts at 32°. *p*-Bromophenyl benzyl sulphide forms small, white crystals, melts at 64—65°, and is soluble in alcohol and ether, less so in light petroleum. *p*-Chlorophenyl benzyl sulphide crystallises in small, white lamellæ and melts at 52—53°. α -Naphthyl methyl sulphide is a colourless liquid and boils at 166—168° under 20 mm. pressure. Benzyl α -naphthyl sulphide crystallises from a mixture of alcohol and water in white lamellæ and melts at 78—80°. T. A. H.

Aminoalcohols. Synthetic at Ephedrines. ERNEST FOURNEAU (*J. Pharm. Chim.*, 1904, [vi], 20, 481—491).—Four isomerides of ephedrine and ψ -ephedrine have been prepared, one of which is most probably the racemic modification of ψ -ephedrine, but has not been resolved into its optically active components. The substituted aminoalcohols described in the paper were prepared by the action of methylamine or dimethylamine on the chloro- or iodo-hydrins of the corresponding unsaturated hydrocarbons.

Phenylmethylaminodimethylcarbinol, $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CMePh} \cdot \text{OH}$, is a colourless, syrupy liquid, boiling at 137° under 33 mm. pressure, slightly soluble in cold, almost insoluble in warm water. The *hydrochloride* and *oxalate* melt at 153° and 158° respectively, and the *aurichloride* decomposes at 148°. The *dibenzoyl* derivative forms brilliant prisms melting at 122°.

Phenylmethylaminoethylcarbinol, $\text{NHMe} \cdot \text{CHMe} \cdot \text{CHPh} \cdot \text{OH}$, forms colourless prisms melting at 60°, and boils at 155—156° under 31 mm. pressure. The odour is that of ψ -ephedrine. It is easily soluble in ether and in alcohol, and dissolves in about its own bulk of water, probably forming a hydrate, which is unstable on warming.

The *hydrochloride* and the *dibenzoyl* derivative melt at 178° and 92° respectively.

Phenyldimethylaminomethylcarbinol, $\text{NMe}_2 \cdot \text{CHMe} \cdot \text{CHPh} \cdot \text{OH}$, forms prismatic needles melting at 47° and boils at 151—152° under 31 mm. pressure. The *hydrochloride*, *picrate*, and *methiodide* melt at 180°, 80°, and 225° respectively. The *benzoyl* derivative, melting at 108°, has an intense anæsthetic action.

Benzylmethylaminomethylcarbinol, $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Ph}) \cdot \text{OH}$, boils at 148° under 22 mm., or at 169° under 40 mm. pressure. Neither the base nor its salts are crystallisable. The *methiodide* and the *dibenzoyl* derivative melt at 148° and 42—43° respectively.

Benzylmethylaminomethylcarbinol is a liquid boiling at 143° under 22 mm. pressure and yielding an *aurichloride* melting at 122°. The liquid *benzoyl* derivative has a bitter taste and anæsthetic action, and forms a *hydrochloride* melting at 165°.

γ -Methylamino- β -phenylpropyl alcohol, $\text{NHMe} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{OH}$, boiling at 145° under 24 mm. pressure, is a liquid, as also are its salts. The corresponding *dimethylamino*-compound is liquid and boils at 136° under 24 mm. or at 153° under 42 mm. pressure. The *hydrochloride*, which is hygroscopic, *aurichloride*, and *methiodide* melt at 288°, 126—127°, and 148° respectively. The *hydrochloride* of the *benzoyl*

derivative has local anæsthetic action, melts at 175° , and gives a *mercurichloride* melting at 141° . G. D. L.

Secondary Phenylnitroethanol. M. HOLLEMAN (*Rec. Trav. Chim.*, 1904, 23, 298—300).—Bouveault and Wahl have shown (Abstr., 1902, i, 682) that when benzaldehyde is condensed with nitromethane in presence of sodium methoxide the first product is the compound $\text{OH}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{NO}\cdot\text{ONa}$, which, on addition of sulphuric acid, is decomposed forming the corresponding secondary nitro-alcohol, which is at the same time partially dehydrated furnishing β -nitrostyrene (compare Thiele and Haeckel, Abstr., 1903, i, 160). The nitro-alcohol can be obtained pure by the addition of acetic acid to the reaction mixture in place of sulphuric acid; it is a bright yellow, viscous liquid, which, when slightly warmed, turns brown and is partially changed into β -nitrostyrene. On oxidation with potassium dichromate and sulphuric acid, it yields α -nitroacetophenone.

T. A. H.

***p*-Methoxyphenylethylcarbinol.** CARL HELL and ALEXANDER HOFMANN (*Ber.*, 1904, 37, 4188—4193).—Phenylethylcarbinols prepared by Grignard's synthesis, and containing a *p*-methoxy-group, have been found to be unstable, losing water on distillation to form alkylene derivatives (Abstr., 1904, i, 241, 242). On the other hand, *p*-methoxyphenylethylcarbinol, prepared by the reduction of propionylanisole, has been described by Klages (Abstr., 1902, i, 609) as being volatile without decomposition. The authors have prepared this compound from anisaldehyde and magnesium ethyl bromide, and find that on distillation under reduced pressure partial decomposition takes place, anethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHMe}$, being formed. After twice distilling under the ordinary pressure, pure anethole is obtained. The decomposition takes place slowly even in the cold. It was not found possible to prepare Klage's phenylurethane derivative, the carbinol yielding only *s*-diphenylcarbamide with phenylcarbimide. C. H. D.

Intramolecular Atomic Rearrangements in Benzpinacones. P. J. MONTAGNE (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 271—275).—When 4 : 4' : 4'' : 4'''-tetrachlorobenzpinacone, obtained by reduction of 4 : 4'-dichlorobenzophenone, is heated with acetyl chloride, tetrachlorobenzpinacolin is formed, which, when boiled with alcoholic potassium hydroxide, forms trichlorotriphenylmethane and *p*-chlorobenzoic acid. Since the trichlorotriphenylmethane obtained is identical with the product obtained from *p*-leucaniline, it is concluded that the intermediate product, demanded by Nef's hypothesis as applied to the formation of a pinacoline from a pinacone, is an impossibility.

In the transformation of $\alpha\beta$ -glycols into aldehydes, an intramolecular rearrangement occurs, which cannot be explained by any normal intermediate reaction. It has not, however, been decided as to whether this atomic migration takes place with the $\alpha\beta$ -glycols themselves, or whether the oxides are formed first and then undergo intramolecular rearrangement. A. McK.

Derivatives of Amino-acids. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1904, **43**, 68—71).—Amino-acids yield characteristic derivatives when their alkaline solutions are thoroughly shaken with ethereal solutions of 4-nitrotoluene-2-sulphonic chloride.

4-Nitrotoluene-2-sulphoglycine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallises from hot water in long needles or large, thin plates melting at 180° (corr.). The barium salt crystallises from water in long prisms.

r-4-Nitrotoluene-2-sulphoalanine,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$,
 crystallises in slender needles melting at 96° . One part of the acid dissolves in 690 of water at 12° .

r-4-Nitrotoluene-2-sulphoglutamic acid,
 $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$,
 crystallises in long, slender needles, melts at 160 — 161° (corr.), and readily forms supersaturated solutions. The barium salt crystallises from water in colourless prisms. J. J. S.

Nitriles of Hydroxy- and Amino-carboxylic Acids. HANS TH. BUCHERER (*Ber.*, 1904, **37**, 4510—4513. Compare Knoevenagel, *Abstr.*, 1904, i, 981, 989, 994, 1024, 1027, 1028).—A claim for priority. C. H. D.

Action of an Ammoniacal Solution of Silver Oxide on Salicylic Acid and Salicylaldehyde. HEINRICH BRUNNER (*Chem. Zeit.*, 1904, **28**, 1123—1124. Compare *Abstr.*, 1902, i, 452).—*iso*-Salicylic acid, previously described (*loc. cit.*), does not exist. A nitro-compound is formed when an ammoniacal solution of silver oxide acts on salicylic acid. A. McK.

A New Preparation of Alkylthiosalicylic Acids. IRMA GOLDBERG (*Ber.*, 1904, **37**, 4526—4527).—The sodium salt of thiophenol reacts with potassium *o*-chlorobenzoate at 220 — 230° in presence of a small quantity of copper to form phenylthiosalicylic acid: $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CO}_2\text{K} + \text{C}_6\text{H}_5 \cdot \text{SNa} = \text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{SPh} + \text{NaCl}$. The product is identical with the acid obtained by Graebe and Schultess (*Abstr.*, 1891, 1058) from thiophenol and *o*-diazobenzoic acid chloride.

p-Tolylthiosalicylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_4\text{Me}$, from *p*-thiocresol, melts at 215 — 216° (corr.) and dissolves readily in alcohol, benzene, acetic acid, or ether, very sparingly in cold water or light petroleum. The solution in concentrated sulphuric acid is yellow, and shows a green fluorescence on warming (formation of a thioxanthone).

β -Naphthylthiosalicylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_{10}\text{H}_7$, from β -thionaphthol, crystallises from alcohol in glistening, white leaflets and melts at 200 — 201° (corr.). The solution in concentrated sulphuric acid is yellow, with slight green fluorescence. C. H. D.

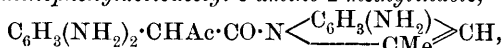
Reduction Products of Ethyl 2 : 4-Dinitrophenylacetoacetate. ARNOLD REISSERT and HANS HELLER (*Ber.*, 1904, **37**, 4364—4379).—Ethyl 2 : 4-dinitrophenylacetoacetate (compare Heckmann, *Abstr.*,

1884, 178) is conveniently prepared by the interaction of ethyl sodio-acetoacetate with chlorodinitrobenzene in cold alcoholic solution, the mixture being left for two weeks. When reduced with stannous chloride under special experimental conditions, a mixture is obtained of 1 part of *ethyl aminomethylindolecarboxylate* and 5 parts of the ester-amide next described. *Ethyl 2:4-diaminophenylacetoacetyl-2:4-diaminophenylacetoacetate*,

$C_6H_3(NH_2)_2 \cdot CHAc \cdot CO \cdot NH \cdot C_6H_3(NH_2) \cdot CHAc \cdot CO_2Et$, crystallises from alcohol in colourless needles, turns brown at 212° , and melts and decomposes at 217.5° ; it gives a green coloration with ferric chloride. The *hydrochloride* crystallises in plates, the *sulphate* in glistening platelets, the *metallic* salts not being well characterised. The *penta-acetyl* derivative, $C_{21}H_{21}O_5N_4Ac_5$, crystallises in colourless needles melting at 167° ; the *diacetyl* derivative, which is prepared in the form of the sodium salt by warming the penta-acetyl derivative with dilute sodium hydroxide, crystallises in colourless, granular crystals which decompose at $249-250^\circ$.

The *tribenzoyl* derivative, prepared by benzoylating in presence of an alkaline hydroxide at 0° , melts at 167.5° ; on prolonged boiling with alcoholic alkali, the *dibenzoyl* derivative is formed, crystallising from alcohol in colourless plates melting at 201.5° . The *tetrazo*-derivative of the ester-amide, $C_{22}H_{20}O_5N(N_2Cl)_2 \cdot NH_2, HCl, 2H_2O$, crystallises in glistening, green plates and couples with β -naphthol to form a dark red and with resorcinol to form a bright red dye.

2':4'-Diaminophenylacetoacetyl-6-amino-2-methylindole,



prepared by the action of 30 per cent. sodium hydroxide in sealed tubes at 100° on the ester-amide, forms bright yellow crystals, which rapidly become blue in the air and decompose with great violence at 142.5° . The *tribenzoyl* derivative crystallises in colourless crystals decomposing at 138° . *Ethyl 6-amino-2-methylindole-3-carboxylate* is formed when the ester-amide is heated at $230-240^\circ$; it crystallises from alcohol in colourless, glistening plates melting at 185° ; the *hydrochloride* crystallises in plates, the *acetate* in rhombohedra which sublime at 340° without decomposing.

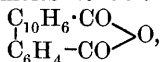
6-Amino-2-methylindole, prepared by the action of sulphuric acid on the foregoing compound, crystallises from alcohol in well formed prisms melting at 82° ; these decompose very rapidly even in a vacuum. The *picrate* crystallises in dark yellow plates melting at 192° ; the *benzoyl* compound forms colourless plates and melts at 209° ; the *acetyl* derivative melts at 180.5° . The structure of ethyl 6-amino-2-methylindolecarboxylate was confirmed by the replacement of the amino-group through the diazo-reaction and the hydrazine-groups by hydrogen, when the ethyl methylindole-3-carboxylate described by Nef was obtained (Abstr., 1892, 140).

E. F. A.

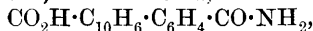
Chrysodiphenic Acid. [*2'-Phenylnaphthalene-1:2'-dicarboxylic Acid.*] CARL GRAEBE and ROBERT GNEHM, jun. (*Annalen*, 1904, 335, 113—121. Compare Abstr., 1902, i, 679).—When strongly heated, chrysodiphenic acid yields chrysoketone and traces of β -phenyl-

naphthalene; the *silver* salt, $C_{13}H_{10}O_4Ag_2$, is obtained as a colourless precipitate.

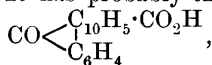
The *methyl hydrogen* ester, $CO_2H \cdot C_{10}H_6 \cdot C_6H_4 \cdot CO_2Me$, formed by the action of methyl alcohol and hydrogen chloride on the acid or by the action of methyl alcohol on the anhydride, crystallises in prisms, melts at 124° , and forms the *silver* salt, $C_{10}H_{13}O_4Ag$. The isomeric *methyl hydrogen* ester, $CO_2Me \cdot C_{10}H_6 \cdot C_6H_4 \cdot CO_2H$, formed by partial hydrolysis of the dimethyl ester, melts at 171.5° . The *dimethyl* ester crystallises in plates and melts at 90° . The anhydride,



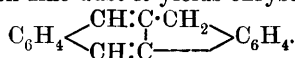
crystallises in colourless needles, melts at 146° , when strongly heated yields chrysoketone, and, with ammonia, forms the amic acid,



which melts at 220° . Chrysoketonecarboxylic acid, which, along with a small amount of its isomeride, is formed by the action of sulphuric acid on chrysodiphenic acid, melts at 283° , is identical with Graebe and Hönigsberger's acid (Abstr., 1900, i, 506), and yields only traces of an ester when heated on the water-bath with methyl alcohol and hydrogen chloride. It has probably the constitution



but when heated with zinc dust it yields chrysfluorene,



G. Y.

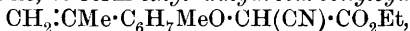
Condensing Action of Organic Bases. EMIL KNOEVENAGEL (*Ber.*, 1904, **37**, 4461—4463).—A *résumé* of the literature on the condensations of aldehydes, ketones, esters, and keto-esters with ammonia, or primary or secondary bases, and an introduction to the following papers.

G. Y.

Condensing Action of Organic Bases. EMIL KNOEVENAGEL and SIEGBERT MOTTEK (*Ber.*, 1904, **37**, 4464—4476).—In presence of diethylamine, ethyl cyanoacetate and methyl fumarate react at the ordinary temperature, forming ethyl dimethyl cyanotricarballylate, $CO_2Me \cdot CH_2 \cdot CH(CO_2Me) \cdot CH(CN) \cdot CO_2Et$, which is a yellow oil, distils at 190 — 210° under 16 mm. pressure, and when hydrolysed with hydrochloric acid yields tricarballylic acid.

In presence of diethylamine and ethylamine, or, with poorer yield, piperidine, methyl fumarate and ethyl malonate form dimethyl diethyl propanetetra-carboxylate, which boils at 198 — 210° under 18 mm. pressure and is hydrolysed by hydrochloric acid to tricarballylic acid.

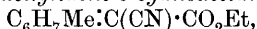
Carvone combines with ethyl cyanoacetate, in presence of diethylamine or piperidine, to form *ethyl dihydrocarvonylcianoacetate*,



which is a yellow, viscid oil, boils at 150 — 151° under about 1 mm. pressure, has a bitter, unpleasant flavour, and is almost insoluble in water. The *oxime*, $C_{15}H_{22}O_3N_2$, crystallises in matted needles, melts at 109 — 111° , or, after recrystallisation from 70 per cent. alcohol, at

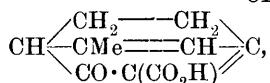
119—121°. Hydrolysis of the ester leads to the formation of *dihydro-carboxylacetic acid*, $\text{CH}_2\text{:CMe}\cdot\text{C}_6\text{H}_7\text{MeO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is a brown, viscid oil; it decomposes on distillation under reduced pressure and yields a flocculent *silver* salt, $\text{C}_{12}\text{H}_{17}\text{O}_3\text{Ag}$.

Ethyl 1-methylcyclohexenylidene-3-cyanoacetate,



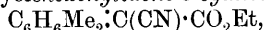
formed by the action of ethyl cyanoacetate on methylcyclohexenone in presence of diethylamine or of piperidine, melts at 55—57° to a yellow oil, which distills at 178—190° under 12 mm. pressure. The ester is stable towards acids, but is easily attacked by alkalis; it is hydrolysed by 10—15 per cent. potassium hydroxide solution to methylcyclohexenone and malonic acid; hydrolysis with dilute sodium carbonate or 2—5 per cent. potassium hydroxide solution

leads to the formation of the *acid*, $\text{CH}_2\left\langle\begin{array}{c} \text{CH}_2\text{---C---CH}_2 \\ \text{CH}_2\text{---C}\equiv\text{CH} \\ \text{CH}_2\text{---C}\equiv\text{C(CO}_2\text{H)} \end{array}\right\rangle\text{CO}$ or



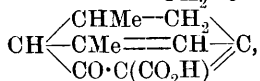
which separates from alcohol in yellow crystals, melts at 147—148.5°, and yields methylcyclohexenone and potassium malonate when boiled with 10 per cent. potassium hydroxide solution. The *ammonium*, *ferric*, and *silver*, $\text{C}_{10}\text{H}_9\text{O}_3\text{Ag}$, salts are described; two *methyl* esters, $\text{C}_{11}\text{H}_{12}\text{O}_3$, melting at 37—39° and 64—66° respectively, are obtained by the action of methyl iodide on the silver salt.

Ethyl 1:5-dimethylcyclohexenylidene-3-cyanoacetate,



obtained by the action of ethyl cyanoacetate on dimethylcyclohexenone in the presence of diethylamine, separates from alcohol in yellow crystals, melts at 57—58°, boils at 192—195° under 16 mm. pressure, and is stable towards acids. When boiled with 10 per cent. potassium hydroxide solution, the ester yields potassium malonate and dimethylcyclohexenone. Hydrolysis of the ester with dilute sodium carbonate or very dilute potassium hydroxide solution leads to the

formation of the *acid*, $\text{CHMe}\left\langle\begin{array}{c} \text{CH}_2\text{---C---CH}_2 \\ \text{CH}_2\text{---C}\equiv\text{CH} \\ \text{CH}_2\text{---C}\equiv\text{C(CO}_2\text{H)} \end{array}\right\rangle\text{CO}$ or



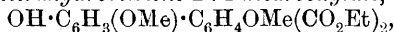
which is a yellow, crystalline substance, melts at 135—136°, and is easily soluble in alcohol, ether, or chloroform, but is insoluble in water. The *ammonium* salt melts and decomposes at 164°; the *silver* salt, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Ag}$, is obtained as a white powder. G. Y.

Condensation of Vanillin with Ethyl Acetoacetate and its Analogues. EMIL KNOEVENAGEL and FRIEDRICH ALBERT (*Ber.*, 1904, 37, 4476—4482).—Vanillin reacts with 1 or 2 mols. of ethyl acetoacetate, or 1 or 2 mols. of acetylacetone, or with ethyl malonate in presence of diethylamine, or more energetically in presence of

piperidine, to form the following condensation products. *Ethyl vanillylideneacetoacetate*, $C_{14}H_{16}O_6$, crystallises from dilute alcohol, melts at $120-121^\circ$, and is soluble in aqueous alkali hydroxides, but insoluble in acids. When warmed with hydroxylamine hydrochloride in alcoholic solution, it forms 5-keto-3-methyl-4-vanillylidene-4:5-dihydroisooxazole, $\begin{matrix} \text{O} \cdot \text{CO} \cdot \\ | \\ \text{N} : \text{C} \cdot \text{Me} \end{matrix} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{OH}$, which melts at 220° and is soluble in aqueous alkali hydroxides, but not in acids.

Ethyl vanillylidenebisacetoacetate, $C_{20}H_{26}O_8$, melts at $163-164^\circ$ and decomposes when heated above its melting point. The oxime, $C_{20}H_{27}O_8N$, forms white crystals and melts at $198-200^\circ$, or, after recrystallisation from alcohol, at $210-220^\circ$.

Hydrolysis of the ester with dilute alkali hydroxides leads to the formation of vanillylidenebisacetoacetic acid, $C_{16}H_{18}O_8$, which melts and decomposes at $127-128^\circ$. Ethyl 1-keto-5-methyl-3-p-hydroxy-m-methoxy-phenyl-1:2:3:4-tetrahydrobenzene-2:4-dicarboxylate,



obtained by the action of hydrogen chloride on the ester in alcoholic solution, crystallises in white needles and melts at $146-147^\circ$.

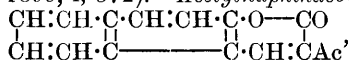
Vanillylideneacetylacetone, $C_{13}H_{14}O_4$, crystallises in thin, yellow needles and melts at 135° . Vanillylidenebisacetylacetone, $C_{18}H_{22}O_6$, crystallises in slender, white needles and melts, when crude, at $150-151^\circ$, or, after recrystallisation, at $170-171^\circ$. The action of hydroxylamine hydrochloride on vanillylidenebisacetylacetone in dilute alcoholic solution leads to the formation of the oxime of 1-keto-2:4-di-acetyl-5-methyl-3-p-hydroxy-m-methoxy-phenyl-1:2:3:4-tetrahydrobenzene, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{C}_6\text{H}_4\text{MeAc}_2 \cdot \text{N} \cdot \text{OH}$, which melts at $223-224^\circ$.

Ethyl vanillylidenemalonate, $C_{15}H_{18}O_6$, melts at 110° . Vanillylidene-malonic acid melts at 212° . G. Y.

Condensation of Cinnamaldehyde with Ethyl Malonate and Acetylacetone. EMIL KNOEVENAGEL and ALBERT HERZ (*Ber.*, 1904, **37**, 4483—4484).—Ethyl cinnamylidenemalonate, $C_{23}H_{30}O_8$, obtained by the condensation of cinnamaldehyde with ethyl malonate in presence of piperidine, melts at 36° to a mobile oil which boils at 218° under 9 mm. pressure.

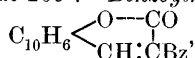
Cinnamylidenemalonate, $C_{14}H_{14}O_3$, forms yellow crystals, melts at 102.5° , and boils at 191° under 17 mm., or, almost without decomposition, at 304° under the ordinary pressure. G. Y.

Condensation of β -Hydroxy- α -naphthaldehyde with Ethyl Acetoacetate and its Analogues. EMIL KNOEVENAGEL and FRITZ SCHRÖDER (*Ber.*, 1904, **37**, 4484—4491. Compare Gattermann and Horlacher, *Abstr.*, 1899, i, 372).—Acetylnaphthacoumarin,



obtained by warming β -hydroxy α -naphthaldehyde and ethyl acetoacetate with piperidine in alcoholic solution, crystallises in leaflets, melts at 186° , and dissolves in concentrated sulphuric acid to a blood-red, or in 10 per cent. aqueous potassium hydroxide to a brownish-red

solution. The *phenylhydrazone*, $C_{21}H_{16}O_2N_2$, crystallises in matted, scarlet needles and melts at 209° . *Benzoylnaphthacoumarin*,



obtained from β -hydroxy- α -naphthaldehyde and ethyl benzoylacetate, crystallises in yellow needles and melts at 208° .

Ethyl naphthacoumarincarboxylate, $C_{10}H_6 \begin{array}{l} \diagup O \text{---} CO \\ \diagdown CH : C \cdot CO_2Et \end{array}$, obtained from β -hydroxy- α -naphthaldehyde and ethyl malonate, crystallises in matted, white needles, melts at 115° , and forms blue, fluorescent solutions. Hydrolysis of the ester leads to the formation of the *carboxylic acid*, $C_{14}H_8O_4$, which is also formed by the action of malonic acid on β -hydroxy- α -naphthylideneaniline. It melts at 231° and gives an intense yellow coloration with concentrated sulphuric acid.

β -Hydroxy- α -naphthylideneacetylacetone, $OH \cdot C_{10}H_6 \cdot CH : C(COMe)_2$, crystallises in yellow needles and melts at 137° . When shaken with glacial acetic acid, it yields a yellow, flocculent *substance*, which melts and decomposes at $200\text{--}210^\circ$.

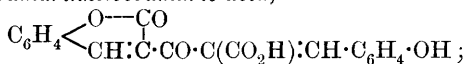
The action of ethyl cyanoacetate on β -hydroxy- α -naphthaldehyde in presence of piperidine in alcoholic solution leads to the formation of *ethyl cyanonaphthacoumarincyanoacetate*, $C_{19}H_{11}O_4N_2$, which crystallises in yellow needles, melts and decomposes at 283° , and is decomposed by boiling glacial acetic acid to a yellow nitrogenous *substance* melting at 112° .

G. Y.

Condensation of Salicylaldehyde and of β -Hydroxy- α -naphthaldehyde with Ethyl Acetonedicarboxylate. EMIL KNOEVENAGEL and E. LANGENSIEPEN (*Ber.*, 1904, **37**, 4492—4496).—Salicylaldehyde (1 mol.) and ethyl acetonedicarboxylate (1 mol.) condense in presence of piperidine to form *ethyl coumarinketoacetate*,

$C_6H_4 \begin{array}{l} \diagup O \text{---} CO \\ \diagdown CH : C \cdot CO \cdot CH_2 \cdot CO_2Et \end{array}$ which crystallises in slender, white needles, melts at 104° , and, on hydrolysis, yields the *acid*, $C_{10}H_6O_4$; this crystallises in colourless needles and melts at 187° .

Dicoumarin ketone, $C_{19}H_{10}O_5$, is formed by condensation of ethyl coumarinketoacetate with salicylaldehyde, or of ethyl acetonedicarboxylate (1 mol.) with salicylaldehyde (2 mols.). It forms small, white crystals and melts at 234° . The *oxime*, $C_{19}H_{11}O_5N$, crystallises in long, glistening needles and melts at 251° . When warmed with aqueous potassium hydroxide or sodium carbonate, dicoumarin ketone dissolves to a red solution, addition of hydrochloric acid to which precipitates *coumarinketocoumaric acid*,



the acid crystallises in small, white needles, melts at $259\text{--}260^\circ$, and yields dicoumarin ketone when treated with acetic anhydride.

Ethyl naphthacoumarinketoacetate, $C_{10}H_6 \begin{array}{l} \diagup O \cdot CO \\ \diagdown CH : C \cdot CO \cdot CH_2 \cdot CO_2Et \end{array}$, forms a yellow, crystalline mass, melts at $151\text{--}152^\circ$, and, on hydrolysis,

yields naphthacoumarincarboxylic acid, $C_{14}H_{14}O_4$, which melts at 232° (see foregoing abstract). G. Y.

Condensation of Salicylaldehyde with Ethyl Cyanoacetate, Ethyl Benzoylacetate, or Acetylacetone. EMIL KNOEVENAGEL and ROBERT ARNOT (*Ber.*, 1904, **37**, 4496—4502. Compare Abstr., 1898, i, 406; 1899, i, 116).—Salicylaldehyde reacts with ethyl cyanoacetate, in presence of piperidine, to form ethyl salicylidenebiscyanoacetate (Beccari, Abstr., 1902, i, 371), which melts at 139 — 140° , yields ammonia and salicylaldehyde when boiled with dilute alkali hydroxides, and when boiled with water is decomposed to a white substance, which melts at 85° , and a product which melts and decomposes at 180 — 250° . β -2-Hydroxyphenylpropane- $\alpha\alpha$ -tricarboxylic anhydride, $\begin{array}{c} \text{CH}:\text{CH}\cdot\text{C}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}-\text{O} \\ | \qquad \qquad | \\ \text{CH}:\text{CH}\cdot\text{C} \qquad \text{CH}\cdot\text{CH}_2\cdot\text{CO} \end{array}$, formed when ethyl salicylidenebiscyanoacetate is boiled with dilute hydrochloric acid, crystallises in white leaflets and melts at 85 — 86° .

Benzoylcoumarin, $C_{16}H_{10}O_3$, obtained by the condensation of salicylaldehyde and ethyl benzoylacetate in presence of piperidine, crystallises in white needles and melts at 130° .

Salicylidenebispiperidine, $C_{17}H_{26}ON_2$, formed by the condensation of salicylaldehyde with piperidine, melts at 86 — 87° and, when warmed with ethyl benzoylacetate, yields benzoylcoumarin. The *oxime*, $C_{16}H_{11}O_3N$,

of the latter crystallises in white needles and melts at 148 — 150° .

Salicylideneacetylacetone, $C_{12}H_{12}O_3$, obtained by condensation of salicylaldehyde with acetylacetone, forms white crystals, melts at 85° , and forms a yellow *additive* compound with bromine, and a *potassium* salt which crystallises in glistening, green needles. The *oxime*, $C_{12}H_{13}O_3N$, crystallises in white leaflets and melts at 110° . Addition of dilute acids to the alcoholic solution of salicylideneacetylacetone results in the formation of a white, crystalline *compound*, $C_{15}H_{16}O_3$, which melts and decomposes at 105° and, on recrystallisation from hot water, forms yellow needles which melt at 109° . The action of dilute acids on the substance melting at 105° , or prolonged boiling of the substance melting at 109° with water, leads to the formation of a *compound* which melts and decomposes at 70 — 75° . The action of dilute nitric acid at 130° under pressure on the substance melting at 105° , leads to the formation of a yellow nitrogenous *substance* which melts at 113° and forms an explosive *potassium* salt crystallising in yellow needles. The *oxime*, $C_{15}H_{16}O_3\cdot NOH$, melts at 118° ; the *phenylhydrazone* melted, when impure, at 125 — 130° .

G. Y.

Condensation of Aliphatic Nitro-compounds with Aromatic Aldehydes by means of Organic Bases. EMIL KNOEVENAGEL and LEONHARD WALTER (*Ber.*, 1904, **37**, 4502—4510).—Aromatic aldehydes (benzaldehyde, piperonal, anisaldehyde, vanillin) form condensation products with primary aliphatic nitro-compounds (nitromethane, nitroethane, phenylnitromethane) in presence of amylamine, ethyl-

amine, or methylamine carbonate, less rapidly in presence of piperidine or diethylamine. The following new compounds are described:

Anisylidenenitromethane, $C_9H_9O_3N$, crystallises in slender, yellow needles or plates and melts at 86° . *Vanillylidenenitromethane*, $C_9H_9O_4N$, melts at 165° .

Piperonylidenenitroethane, $C_{10}H_9O_4N$, crystallises in golden needles and melts at 98° . *Anisylidenenitroethane*, $C_{10}H_{11}O_3N$, forms long, yellow, prismatic crystals and melts at 48° .

Phenylbenzylidenenitromethane, $C_{14}H_{11}O_2N$, crystallises in yellow leaflets and melts at 75° .

Phenylpiperonylidenenitromethane, $C_{15}H_{11}O_4N$, forms yellow crystals and melts at 124° .

Phenylanisylidenenitromethane, $C_{15}H_{13}O_3N$, crystallises in broad, golden needles and melts at 151° . G. Y.

Oxidising Chlorination of *o*-Hydroxybenzaldehyde and of *p*-Hydroxybenzaldehyde. HEINRICH BILTZ (*Ber.*, 1904, 37, 4448).—An analytical correction (compare Abstr., 1904, i, 1021).

W. A. D.

The Occurrence of Vanillin. EDMUND O. VON LIPPMANN (*Ber.*, 1904, 37, 4521—4522).—The odour of vanillin is frequently noticeable in the neighbourhood of saw-mills. A shaving of wood taken in one case when the odour was exceptionally strong yielded sufficient vanillin on extraction with ether to allow of recrystallisation and identification. Vanillin has been previously recognised in wood (compare Seidel, *Zeit. angew. Chem.*, 1898, 876; Bräutigam, Abstr., 1901, i, 93; Grafe, this vol., i, 23).

C. H. D.

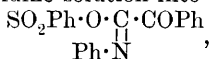
Hydrogenation of Aromatic Ketones by means of Reduced Nickel. New Method of Synthesising Aromatic Hydrocarbons. GEORGES DARZENS (*Compt. rend.*, 1904, 139, 868—870).—When aromatic ketones of the type $COPhR$ are directly hydrogenated at 190 — 195° in the presence of nickel obtained by reducing nickel oxide at 300° , the reaction proceeds according to the following equation: $COPhR + 2H_2 = CH_2PhR + H_2O$; if, however, the nickel employed has been obtained by reducing the oxide at a temperature below 300° , it behaves as a more active catalyst (compare Sabatier and Senderens, Abstr., 1903, i, 733), and the corresponding hexahydro-derivative of the benzene homologue is obtained. The following homologues of benzene were prepared: ethylbenzene, boiling at 136 — 137° , from acetophenone; *p*-methylethylbenzene, boiling at 158 — 162° , from *p*-tolyl methyl ketone; *p*-ethyl-*tert*-butylbenzene, from *p*-butylacetophenone, boils at 209 — 213° and has an odour similar to that of carrots; and butylbenzene, boiling at 180° , from benzylacetone. M. A. W.

Beckmann's Rearrangement by means of Benzene Sulphonic Chloride in the Presence of Alkali or Pyridine. ALFRED WERNER and A. PIGUET (*Ber.*, 1904, 37, 4295—4315).—The Beckmann reaction under the influence of benzenesulphonicchloride proceeds well in pyridine solution, and the isolation of the primary products is more readily effected than when an alkaline solution is used.

In the case of α - or *o*-diketonemonoximes, the rearrangement may

take place in two ways; the hydroxyl at first attached to nitrogen becoming attached either to the carbon atom immediately linked with the nitrogen, or to the carbon atom connected with the ketonic oxygen. The second form of the reaction occurs especially with the oximes of cyclic *o*-diketones.

γ -Benzilmono-oxime is converted by benzenesulphonic chloride in sodium hydroxide or pyridine solution into the compound



which crystallises from alcohol in colourless, prismatic needles melting at 114° , and may be regarded as the benzenesulphonic ester of the pro-

duct of the Beckmann rearrangement, $\text{OH}\cdot\underset{\text{Ph}\cdot\text{N}}{\underset{\text{||}}{\text{C}}}\cdot\text{COPh}$ Alcoholic potass-

ium hydroxide converts it into phenylcarbylamine and benzoic and benzenesulphonic acids; dilute sulphuric acid forms aniline, benzonitrile, and benzenesulphonic acid. An attempt to synthesise the compound from benzoylformanilide and benzenesulphonic chloride was unsuccessful.

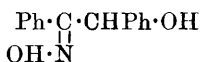
Under the same conditions, α -benziloxime yields the compound $\text{Ph}\cdot\underset{\text{N}\cdot\text{COPh}}{\underset{\text{||}}{\text{C}}}\cdot\text{O}\cdot\text{COPh}$, crystallising from acetic acid in large, colourless prisms

melting at 95° , and yielding ammonia and benzonitrile or benzoic acid on hydrolysis. It is therefore the benzoyl ester of the normal product, benzoic acid being produced by a rearrangement of the second type. The stereochemical formulæ proposed for the benziloximes by Beckmann and Köster (Abstr., 1893, i, 474) are thus confirmed (compare Hantzsch and Werner, Abstr., 1890, 970).

Both the α - and β -oximes of benzoylformic acid yield only benzonitrile; deoxybenzoinoxime yields phenylacetanilide, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, crystallising in colourless prisms and melting at 117° . Benzophenone-oxime yields only benzanilide.

Both *anti*- and *syn*-benziladoximes yield benzonitrile. Camphoroxime yields campholenonitrile.

α -Benzoinoxime yields benzonitrile and benzaldehyde (rearrangement of the second type). β -Benzoinoxime behaves normally, yielding phenylglycollanilide, $\text{NHPh}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{OH}$. The formulæ to be assigned to the oximes are therefore: α -oxime, $\text{Ph}\cdot\underset{\text{N}\cdot\text{OH}}{\underset{\text{||}}{\text{C}}}\cdot\text{CHPh}\cdot\text{OH}$; β -oxime,



α -Nitroso- β -naphthol reacts with either benzenesulphonic chloride or sulphuryl chloride in pyridine solution to form *o*-cyanocinnamic acid, a reaction of the second type. In similar manner, phenanthraquinone-oxime yields 2-cyanodiphenyl-2'-carboxylic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, crystallising from benzene in colourless prisms and melting at 170 – 172° ; the *methyl* ester forms long double-pyramids and melts at 79 – 80° . 2-Nitrophenanthraquinoneoxime yields a nitro-2-cyanodiphenyl-2'-carboxylic acid, crystallising in pale yellow prisms melting at 194 – 195° ; the *methyl* ester forms colourless needles and melts at 123 – 124° . 2:7-Dinitrophenanthraquinoneoxime yields a dinitro-2-cyanodiphenyl-

2'-carboxylic acid, crystallising in colourless leaflets melting at 217—218°; the methyl ester forms small prisms melting at 149—150°. Retenequinoneoxime yields the mononitrile of methylisopropyldiphenic acid, $C_{18}H_{17}O_2N$, forming small, colourless crystals melting at 195°.

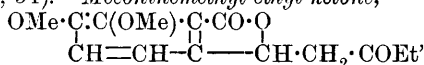
Acenaphthaquinoneoxime yields the imide of naphthalic acid, $C_{12}H_7O_3N$, crystallising in small, colourless needles and melting at 290—291°. The solution in concentrated sulphuric acid shows an intense blue fluorescence. C. H. D.

Condensation of Diphenic Anhydride with Toluene. HANS PICK (*Monatsh.*, 1904, 25, 979—986. Compare Götz, Abstr., 1902, i, 372).—Fluorenone-5-carboxylic acid and *p*-toluoyl-5-fluorenone are formed when diphenic anhydride in toluene solution is warmed with aluminium chloride.

4-*p*-Toluoylfluorenone, $\begin{array}{c} \text{CO}-\text{C}:\text{CH}-\text{CH} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}:\text{C}(\text{CO} \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array}$, is better formed by the action of aluminium chloride on fluorenone-5-carboxylic chloride in toluene solution; it crystallises in yellow, prismatic needles, melts at 128°, dissolves in concentrated sulphuric acid to an orange-red solution, and forms a phenylhydrazone, $C_{27}H_{20}ON_2$, which decomposes at 82°. 4-*p*-Methylbenzylfluorene, $\begin{array}{c} \text{CH}_2-\text{C}:\text{CH}-\text{CH} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}:\text{C}(\text{CH}_2 \cdot \text{C}_7\text{H}_7) \cdot \text{CH} \end{array}$, obtained by heating toluoyl-5-fluorenone with zinc dust, crystallises in white needles and melts at 72°.

The condensation of fluorenone-4-carboxylic chloride with anisole in presence of aluminium chloride leads to the formation of 4-*p*-methoxybenzylfluorenone, $\begin{array}{c} \text{CO}-\text{C}:\text{CH}-\text{CH} \\ | \quad | \\ \text{C}_6\text{H}_4 \cdot \text{C}:\text{C}(\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}) \cdot \text{CH} \end{array}$, which forms white crystals and melts at 95°. G. Y.

Condensations of *o*-Aldehydcarboxylic Acids with Ketones. ALFRED LUKSCH (*Monatsh.*, 1904, 25, 1051—1064. Compare Zink, Abstr., 1902, i, 34).—*Meconinemethyl ethyl ketone*,



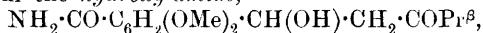
formed by the action of opianic acid on methyl ethyl ketone in aqueous sodium hydroxide solution at 35°, crystallises in white needles, melts at 128—132°, is soluble in hot water or alcohol, dissolves in boiling aqueous alkali carbonates, and is decomposed by hot aqueous potassium hydroxide. The oxime forms small, glistening crystals and melts at 109—112°.

Meconinemethyl propyl ketone, $C_{10}H_9O_4 \cdot \text{CH}_2 \cdot \text{COPr}^a$, crystallises in small needles, melts at 91—95°, is soluble in warm water, alcohol, ether, benzene, chloroform, or glacial acetic acid, and is decomposed by warm aqueous potassium hydroxide. The oxime melts at 153—157°. *Meconinemethyl isopropyl ketone*, $C_{10}H_9O_4 \cdot \text{CH}_2 \cdot \text{COPr}^b$, melts at 88—91° and is soluble in hot water or alcohol. With hydroxylamine hydrochloride in alcoholic solution, or with hydroxylamine in alcoholic sodium hydroxide solution, it forms the oxime of the "pseudo-acid" (compare Fulda, Abstr., 1900, i, 36), $C_{15}H_{19}O_5N$, which crystallises in matted, white

needles, melts at 110° , and is soluble in warm water, alcohol, or benzene or in cold acetone, chloroform, or glacial acetic acid; it has a neutral action towards litmus and dissolves in aqueous alkali hydroxides or carbonates only on warming. When heated to its melting point, it undergoes isomeric change into the *oxime* of the acid, which is also formed by the action of hydroxylamine on the ketone at 100° in alcoholic solution; this oxime crystallises in colourless, glistening, silky needles, melts at 223° , is less soluble in warm water or alcohol than its isomeride, dissolves readily in cold aqueous alkali hydroxides, slowly in cold aqueous alkali carbonates, and can be titrated directly.

The action of aqueous ammonia on meconinemethyl ethyl and meconinemethyl propyl ketones, leads to the formation of yellow, transparent resins.

Meconinemethyl isopropyl ketone and concentrated aqueous ammonia form the *hydroxy-amide*,



which separates in white crystals, melts at $141\text{--}143^{\circ}$, and is easily soluble in hot water or alcohol. It dissolves in concentrated sulphuric acid to a carmine solution, which, when heated, becomes green and finally violet, and yields a brown, flocculent precipitate on addition of water; when boiled with dilute acids, it is hydrolysed with formation of ammonia. When boiled with glacial acetic acid, it yields the *acetyl* derivative, $\text{C}_{17}\text{H}_{23}\text{O}_6\text{N}$, which crystallises in glistening, white leaflets, melts at 187° , and, when treated with sodium nitrite in acetic acid solution, forms meconinemethyl isopropyl ketone. G. Y.

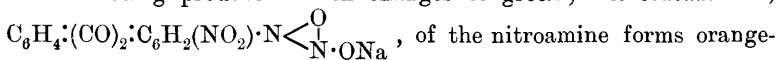
Quinone Imines. III. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1904, **37**, 4605—4609. Compare Willstätter and Mayer, *Abstr.*, 1904, **i**, 511).—Quinonedi-imine, $\text{C}_6\text{H}_6\text{N}_2$, prepared by the oxidation of an ethereal solution of *p*-phenylenediamine by dry silver oxide, separates in colourless needles, which gradually assume a grey to brownish-yellow tint. It forms colourless solutions; it explodes on the addition of concentrated hydrochloric or sulphuric acids, but by careful treatment with pure sulphuric acid its sulphate may be isolated. When quickly heated, it becomes coloured at 75° and melts at about 124° .

Quinonemonoimine, prepared by the oxidation of an ethereal solution of *p*-aminophenol by dry silver oxide, separates in prisms or needles, which, although momentarily colourless, gradually assume a yellowish-grey to brown colour on being exposed to air. It is more unstable than the di-imine and decomposes spontaneously when separated from its ethereal solution, red fumes being evolved. When warmed with dilute sulphuric acid, it is converted into quinone and ammonia; by stannous chloride and hydrochloric acid, it is reduced to *p*-aminophenol. It is more soluble in ether than is the di-imine. With phenol and alkali, it forms a deep blue solution, which, when acidified, turns red, and forms a bluish-green layer when concentrated sulphuric acid is carefully added.

By comparison of those imines with quinone and with Thiele's fulvenes, it appears that, contrary to the current views, the group C:NH is a weaker chromophore than the group C:O or C:C . A. McK.

Nitroamines of the Anthraquinone Series. ROLAND SCHOLL [and, in part, G. SCHNEIDER and F. EBERLE] (*Ber.*, 1904, **37**, 4427—4448).—The nitration of the aminoanthraquinones is remarkable as giving rise to nitroamines as direct products.

On gradually adding at -10° finely powdered 2-aminoanthraquinone to nitric acid of sp. gr. 1.50 which has been freed from nitrous acid by means of carbamide, a mixture of 3-nitro-2-nitroaminoanthraquinone, $C_6H_4:(CO)_2:C_6H_2(NO_2) \cdot NH \cdot NO_2$, and 1:3-dinitro-2-nitroaminoanthraquinone is obtained, which can be resolved into its constituents by recrystallisation from acetone. 3-Nitro-2-nitroaminoanthraquinone separates, on adding water, in yellow crystals, and when pure explodes at a temperature intermediate between 180° and 191° , depending on the rate of heating; when heated with phenol and sulphuric acid, it shows Liebermann's reaction in a modified manner, a brownish-purple solution being produced which changes to green; the sodium salt,



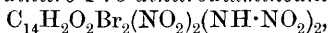
red crystals and decomposes at 245° . On agitating the nitroamino-compound with a mixture of phenol (1 part) and concentrated sulphuric acid (10 parts), it is converted into 3-nitro-2-aminoanthraquinone, which crystallises from xylene and melts at $305-306^{\circ}$; the structure of this follows from its conversion by the diazo-reaction into 2-nitroanthraquinone, which melts at $184.5-185^{\circ}$ (corr.) (compare Kauder, *Abstr.*, 1904, i, 256) and is reducible by ammonium sulphide to 2-aminoanthraquinone.

3-Nitro-1-hydroxyanthraquinone, obtained by passing gaseous nitrous acid into a solution of 3-nitro-2-nitroaminoanthraquinone in fuming nitric acid and boiling the product with alcohol, crystallises from glacial acetic acid in yellow leaflets and melts at $247-248^{\circ}$; its structure was not established, but appears probable in view of the action of fuming nitric acid on 2-aminoanthraquinone (*infra*); 3-amino-1-hydroxyanthraquinone forms slender, red needles and sublimes without melting.

1:3-Dinitro-2-nitroaminoanthraquinone is more soluble in acetone than its congener, separates from ether in bright yellow crystals, and decomposes at 99° ; when agitated with phenol and sulphuric acid, it gives 1:3-dinitro-2-aminoanthraquinone, which crystallises from glacial acetic acid in yellow prisms, melts at $279-280^{\circ}$, and is reduced by ammonium sulphide to 1:2:3-triaminoanthraquinone, which crystallises from nitrobenzene and does not melt at 300° .

3-Nitro-2-nitroamino-1-hydroxyanthraquinone is formed together with 1:3-dinitro-2-nitroaminoanthraquinone when 2-aminoanthraquinone is nitrated with nitric acid of sp. gr. 1.52 at $35-40^{\circ}$; it crystallises from glacial acetic acid in yellowish-red needles and decomposes at 234° .

2:6-Dibromo-4:8-dinitro-1:5-dinitrodiaminoanthraquinone,



prepared by adding finely powdered 2:6-dibromo-1:5-diaminoanthraquinone to colourless nitric acid of sp. gr. 1.52, forms a micro-crystalline powder and decomposes at $142-143^{\circ}$; it is nearly insoluble in all solvents; the crystalline disodium salt, $C_{14}H_2O_{10}N_6Br_2Na_2$, and

the analogous *dipotassium* and *diammonium* salts are anhydrous. 2 : 6-*Dibromo*-4 : 8-*dinitro*-1 : 5-*diaminoanthraquinone*, obtained by denitrating the nitroamino-derivative with phenol and sulphuric acid at the ordinary temperature, separates from phenol or nitrobenzene, in which it is very sparingly soluble, in red crystals having a metallic lustre, and does not melt up to 360°.

2 : 4 : 6 : 8-*Tetrabromo*-1 : 5-*dinitrodiaminoanthraquinone*, prepared by nitrating tetrabromo-1 : 5-diaminoanthraquinone, forms a bright yellow, crystalline powder and explodes at 166°; it is denitrated by simply heating it with alcoholic hydrochloric acid, giving 2 : 4 : 6 : 8-*tetrabromo*-1 : 5-*diaminoanthraquinone*.

2 : 4 : 6 : 8-*Tetranitro*-1 : 5-*dinitrodiaminoanthraquinone*, obtained by nitrating 1 : 5-diaminoanthraquinone with ice-cold nitric acid of sp. gr. 1.52, forms a yellow, crystalline powder and explodes when gently heated or when struck; 2 : 4 : 6 : 8-*tetranitro*-1 : 5-*diaminoanthraquinone* is a dark coloured powder.

W. A. D.

Xanthogen Reaction and its Application to the Terpene and Camphor Series. II. L. A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 988—1052. Compare Abstr., 1904, i, 327).—In the transformation of an alcohol of the terpene or camphor series into a hydrocarbon, isomeric change often takes place. In order to avoid this change, the author applies to such cases the xanthogen reaction, by which means he is able to obtain the hydrocarbon directly corresponding with the alcohol employed.

The first case to which this procedure is applied is that of dihydrocarveol, which is formed by the reduction of *d*-carvone by means of sodium in alcoholic solution. The dihydrocarveol is first converted into sodium dihydrocarvylxanthate, $C_{10}H_7O \cdot CS_2Na$, by acting on its toluene solution with ether and carbon disulphide. The sodium salt is then transformed into the corresponding methyl dihydrocarvylxanthate, which, on dry distillation, decomposes thus: $C_{10}H_{17}O \cdot CS_2Me = C_{10}H_{16} + CSO + CH_3 \cdot SH$. The hydrocarbon thus obtained is a mixture of the two compounds: (1) *l*-limonene and (2) an isomeric substance, to which the author assigns the name *isolimonene* and the structure

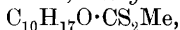
$CHMe \begin{array}{c} \diagup CH=CH \diagdown \\ CH_2 \cdot CH_2 \end{array} CH \cdot CMe : CH_2$. It boils at 172—173° under 754 mm. pressure, has the sp. gr. 0.8374 at 20°/4°, n_D 1.46997, and $[\alpha]_D - 140.11^\circ$. No tetrabromide or nitrosochloride could be obtained. On long boiling in presence of potassium, *isolimonene* undergoes isomeric change into a terpene. With hydrogen bromide, *isolimonene* yields dipentene dihydrobromide melting at 63—64°. All the properties of *isolimonene* indicate that its relation to limonene is similar to that which carvomenthene bears to Δ^2 -menthene.

It is found that dihydrocarveol, obtained by the reduction of *d*-carvone, consists of a mixture of two isomerides, since, under the action of alcoholic ammonia solution, methyl dihydrocarvylxanthate yields two amides: (1) α -*dihydrocarvylxanthamide*, $C_{11}H_{19}ONS$, which separates from light petroleum in colourless crystals melting at 62.5—63.5°; it is extremely readily soluble in ether, alcohol, chloroform, or benzene, and, to a less extent, in light petroleum; has

$[\alpha]_D + 135.33^\circ$ ($c = 9.226$) or 139.03 ($c = 2.916$), and its molecular weight in freezing benzene has the normal value. When treated with excess of concentrated alcoholic potassium hydroxide solution, the α -amide is converted into α -dihydrocarveol, which boils at 222.5 — 222.8° under 749 mm. pressure, and has the sp. gr. 0.9204 at $20^\circ/4^\circ$, $n_D 1.47818$ at 20° , and $[\alpha]_D + 33.86^\circ$. (2) An isomeric amide, which was not obtained pure.

A new method for hydrolysing xanthamides consists in treating them with one of Grignard's organo-magnesium compounds, which acts on the tautomeric (sulphydryl) form of amide, thus: $\text{RO}\cdot\text{C}(\text{SH})\cdot\text{NH} + \text{MeMgI} = \text{RO}\cdot\text{C}(\text{SMgI})\cdot\text{NH} + \text{CH}_4$; the compound thus obtained is then decomposed by excess of water yielding ROH.

The above method is also applied to thujone. The author is of opinion that the thujene obtained by Wallach and the tanacetene of Semmler correspond, not with thujone, but with a product of its isomerisation, isothujone. Starting from thujyl alcohol, he has prepared, by the processes described, methyl thujylxanthate,



which has the sp. gr. 1.0569 at $20^\circ/4^\circ$, $[\alpha]_D + 63.87^\circ$, and $n_D 1.53572$ at 20° . On dry distillation of this methyl ester, part of it undergoes ready decomposition, yielding a hydrocarbon to which the author gives

the name α -thujene and the constitution $\text{CH}_2 \begin{array}{c} \text{CH}-\text{CMe} \\ \diagup \quad \diagdown \\ \text{CPr}^\alpha \cdot \text{CH}_2 \end{array} \text{CH}$;

α -thujene is a colourless, mobile liquid, which boils at 152 — 152.5° under 748 mm. pressure, has the sp. gr. 0.8275 at $20^\circ/4^\circ$, $n_D 1.45042$, and $[\alpha]_D - 4.23^\circ$. It gives no crystalline nitrosochloride, but reacts readily with bromine, hydrogen bromide being evolved. With hydrogen bromide, it yields a dihydrobromide, $\text{C}_{10}\text{H}_{16}\cdot 2\text{HBr}$, melting at 58 — 59° . From its melting point and other properties, this is evidently the dihydrobromide of dipentene, a conclusion confirmed by the fact that on distillation with quinoline it yields limonene; the formation of this dihydrobromide is doubtless the result of isomeric change. α -Thujene is comparatively stable towards the action of heat, and only at 300 — 310° does it show signs of undergoing isomeric change, yielding a compound which is probably isothujene.

The portion of the methyl thujylxanthate which does not readily decompose was subjected to a higher temperature, the product of the distillation being β -thujene, $\text{CH}_2 \begin{array}{c} \text{CH}\cdot\text{CHMe} \\ \diagup \quad \diagdown \\ \text{CPr}^\beta - \text{CH} \end{array} \text{CH}$, which boils at 150 — 151° under 750 mm. pressure and has $[\alpha]_D + 77.43^\circ$, the sp. gr. 0.8248 at $20^\circ/4^\circ$ and 0.8232 at $22^\circ/4^\circ$, and $n_D 1.44842$ at 22° .

That α -thujene is the hydrocarbon corresponding with thujone is confirmed by preparing it from the latter by way of the oxime and amine. Thujoneoxime separates from ether in crystals melting at 53° , is readily soluble in all organic solvents, and has $[\alpha]_D + 107.46^\circ$. On boiling with sodium in alcoholic solution, it is reduced to thujylamine, the hydrochloride of which, $\text{C}_{10}\text{H}_{17}\cdot\text{NH}_2\cdot\text{HCl}$, melts at 260° , and has $[\alpha]_D + 79.36^\circ$, whilst the nitrate forms prismatic crystals melting at 167 — 168° and having $[\alpha]_D + 70.37^\circ$. Thujyltrimethylammonium iodide, $\text{C}_{10}\text{H}_{17}\text{NMe}_3\text{I}$, separates in colourless crystals,

slightly soluble in water or alcohol, and more readily in chloroform; it has $[\alpha]_D + 42.61^\circ$. The action of silver oxide on this compound yields *thujyltrimethylammonium hydroxide*, which forms a viscid, non-crystalline mass, and, on heating, decomposes into trimethylamine and *a*-thujene.

Thujyldimethylamine, $C_{10}H_{17}NMe_2$, is a colourless liquid which boils at 213.5 — 214° , has the sp. gr. 0.8606 at $20^\circ/4^\circ$ and $[\alpha]_D + 148.76^\circ$; its *hydrochloride*, *platinichloride*, *nitrate*, and *picrate* were prepared.

On reducing *isothujone* to *thujamenthol*, converting the latter into the corresponding methyl xanthic ester, $C_{10}H_{19}OCS_2Me$, and distilling this, the hydrocarbon *thujamenthene*, $C_{10}H_{18}$, is obtained as a liquid boiling at 157 — 159° under 750 mm. pressure, and having the sp. gr. 0.8046 at $20^\circ/4^\circ$ and $n_D 1.44591$. *Thujamenthene* is optically inactive, and yields a crystalline nitrosochloride.

Methyl bornylxanthate, $C_{10}H_{17}O \cdot CS_2Me$, obtained in both dextro- and lævo-modifications by the method given above, separates from alcohol in rhombic crystals $[a : b : c = 2.0981 : 1 : 1.4429]$ melting at 56 — 57° , and is soluble in benzene, toluene, chloroform, or ether. The lævo-modification has $[\alpha]_D - 33.38^\circ$ ($c = 13.004$) in benzene and -41.55° ($c = 12.952$) in ethyl acetate, whilst for the dextro-compound the values are $+33.69^\circ$ in benzene and $+41.45^\circ$ in ethyl acetate. On hydrolysis with alcoholic potassium hydroxide solution, these esters give respectively *l*- and *d*-borneols with $[\alpha]_D - 38.23^\circ$ and $+38.39^\circ$. The racemic ester melts at 28.5 — 29° , but does not readily crystallise; it has the sp. gr. 1.0923 at $20^\circ/4^\circ$ and 1.0084 at $25.3^\circ/4^\circ$ and the $n_D 1.54829$ at 26° . On dry distillation, methyl bornylxanthate (from *l*-borneol) yields a new *d*-terpene, $C_{10}H_{16}$, which boils at 149° under 745 mm. pressure, melts at 103 — 104° , and has $[\alpha]_D + 13.77^\circ$. The corresponding lævo-compound has $[\alpha]_D - 12.61^\circ$.

Ethyl bornylxanthate melts at 52 — 53° , forms hemihedral crystals of the rhombic system $[a : b : c = 2.0809 : 1 : 1.4623]$, and dissolves readily in the ordinary solvents. The lævo-form has $[\alpha]_D - 30.54^\circ$ in benzene and -32.96° in toluene, the value for the dextro-form being $+33.35^\circ$ in toluene. The racemic modification melts at 28 — 29° and has the sp. gr. 1.0709 at $20^\circ/4^\circ$ and $n_D 1.54396$.

Bornyldixanthide, $(C_{10}H_{17}O \cdot CS)_2S_2$, is readily obtained by the action of iodine in benzene or ethereal solution on sodium bornylxanthide: $2C_{10}H_{17}O \cdot CS_2Na + I_2 = (C_{10}H_{17}O \cdot CS)_2S_2 + 2NaI$. Both dextro- and lævo-forms melt at 82 — 83° and crystallise from alcohol in long, yellowish-white needles, or, on slow evaporation of a solution in a mixture of alcohol and ether, in long prisms readily forming twin crystals. The dextro-form has $[\alpha]_D + 43.79^\circ$ and the lævo-form -44.12° in benzene. The racemic modification crystallises from ether in yellow needles melting at 81 — 82° .

Bornylxanthamide, $C_{10}H_{17}O \cdot CS \cdot NH_2$, is readily prepared by the action of alcoholic ammonia solution on methyl bornylxanthate. Both the optical antipodes melt at 125 — 126° and separate from a mixture of light petroleum in drusy masses of prismatic crystals. Both exhibit distinct triboluminescence, and dissolve readily in alcohol, ether, benzene, or chloroform. The *d*-amide has $[\alpha]_D + 18.95^\circ$

and the *l*-amide -18.13° in benzene. The racemic form separates in needles or prisms melting at $134.5-135.5^\circ$.

ab-Diphenyl-*c*-bornyliminoxanthide, $C_{10}H_{17}O \cdot CS \cdot S \cdot CPh \cdot NPh$ or $C_{10}H_{17}O \cdot CS \cdot NPh \cdot CSpH$, is prepared by the interaction of sodium bornylxanthate and chlorodiphenylimide, $CPhCl \cdot NPh$. Both *d*- and *l*-forms melt at $87-88^\circ$ and the racemic modification at $89-90^\circ$.

T. H. P.

Crystalline Products of the Ethereal Oil of the Siberian Fir. P. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1096—1108).—The following two compounds have been separated by the author from the ethereal oil of the Siberian Fir (*Abies sibirica*).

(1) *Borneol acetate*, $C_{10}H_{17}OAc$, which crystallises in the rhombic system [$a:b:c=1.44:1:0.67$], melts at 29° and boils at $223-224^\circ$ under 758.3 mm. pressure; it dissolves readily in alcohol, ether, or acetic acid, and to a still greater extent in light petroleum; its heat of combustion is 8540 cal. per 1 gram and it has $[\alpha]_D -45.47^\circ$ at 20° . On hydrolysis, it yields a *borneol*, $C_{10}H_{18}O$, which crystallises from light petroleum in thin, hexagonal plates, melts at 204° , and boils at 210° under 778.8 mm. pressure; it has an aromatic odour and is soluble in the same liquids as its acetate, although to a less degree; its heat of combustion is 95.44 cal. and it has $[\alpha]_D -36.14^\circ$ in alcohol. On oxidation, it yields a *l*-camphor, $C_{10}H_{16}O$, which melts at $188-189^\circ$, boils at 204° under 756.6 mm. pressure, and has $[\alpha]_D -41.11^\circ$ in alcoholic solution; its heat of combustion is the same as that of ordinary Japanese camphor, namely, 9335 cal.

(2) *Camphene*, $C_{10}H_{16}$, which solidifies in needles arranged in feathery masses melting at $40-41^\circ$ and boiling at $159-160^\circ$; its heat of combustion is 10,831 cal. and it has $[\alpha]_D -85^\circ$. T. H. P.

Quercitrin D. H. BRAUNS (*Arch. Pharm.*, 1904, **242**, 561—562).—When dried in the air, quercitrin has the composition $C_{21}H_{20}O_{11} \cdot 2H_2O$. It loses its water completely at 130° , or at 100° under diminished pressure. When the dried substance was exposed to the air, less of this water was taken up again, according as the temperature at which the substance had been dried was higher. C. F. B.

The So-called Scammonose. EMIL VOTOČEK and R. VONDRAČEK (*Ber.*, 1904, **37**, 4615—4616).—Scammonin, obtained from the bulbs of *Convolvulus scammonia*, was converted by baryta into scammonic acid, which yielded a mixture of sugars in which methylpentoses were present. Addition of phenylmethylhydrazine caused the precipitation of rhodosephenylmethylhydrazone. Glucosephenyllosazone was also isolated. *iso*Rhodose was probably also present.

A. McK.

Theory of Dyeing. P. D. ZACHARIAS (*Ber.*, 1904, **37**, 4387—4388. Compare Abstr., 1902, i, 635, 725; 1903, i, 193).—Polemical. A criticism of Biltz's publications (Abstr., 1904, ii, 324, 392) on the mutual

influence of dissolved colloids and the theory of colour ; it includes a claim for priority. E. F. A.

Theory of Dyes. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 871—873. Compare Abstr., 1904, i, 698, 785, 943, 944, 1061 ; this vol., ii, 11, 12).—According to the author's explanation of the difference in structure between the coloured and colourless salts of rosaniline, the amino-groups constitute the auxochromes which, uniting to form a triazine ring, cause the formation of an endothermic group containing ethylenic linkings (the chromophore) at another point of the molecule. The existence in the molecule of two groups possessing such different energies constitutes the cause of colour (compare Helmholtz, *Ann. Physik*, 1875, 154, 582). M. A. W.

Silk and Wool as Dye Producers. HERMANN PAULY and ARTHUR BINZ (*Zeit. Farb. Text.-Ind.*, 1904, 3, 373—374).—The authors consider that the tyrosine which is present in human nails and hair, and in silk and wool, is the cause of the dyeing of these substances when they are immersed in solutions of diazonium salts ; the tyrosine, $\text{OH}\cdot\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, as a phenol, gives rise to a hydroxy-azo-compound. Histidine may behave in a similar way in the case of other physiological substances which interact with diazo-salts. When *p*-phenylenedimethyldiamine is oxidised by bromine water in presence of wool or silk, a dark grey dye is produced on the fibre ; a dye of the same shade is formed by a similar oxidation of the same base in presence of tyrosine, this fact probably showing that the latter substance is the source of the dye on the fibre, and that the latter is analogous to the dyes of the indophenol or oxazine series.

W. A. D.

Behaviour of Coal-tar Dyes towards Starch, Silicic Acid, and Silicates. WILHELM SUIDA (*Monatsh.*, 1904, 25, 1107—1143).—Finely powdered potato starch was shaken with cold filtered aqueous solutions of a number of basic dyes, the liquid decanted, and the starch washed with water until the washings appeared colourless. After this treatment, the starch remained strongly coloured by the most strongly basic dyes, the colour effect decreasing with the basicity until with acid magenta, the trisulphonic acid of rosaniline, the starch, after washing with water, was almost colourless. The amount of the dye absorbed by the starch was extremely small even with the most basic dyes, 5 grams of starch taking up 0.000114 gram of magenta ; the hydrochloric acid of the magenta combines with the mineral constituents of the starch. The potato starch is not coloured by dyes derived from diamines, with the exception of the azo-dyes obtained from diaminostilbene, nor by acid dyes. The behaviour of starch towards basic dyes is similar to that of animal fibres, but towards acid dyes is similar to that of cotton wool.

When shaken in the finely divided state with aqueous solutions of methylene-blue and "diamond fuchsine," sulphur, calcium, strontium, and barium sulphates, calcium, barium, magnesium, manganese, and

lead carbonates, aluminium and zinc oxides, and aluminium phosphate remained uncoloured, whilst kaolin, talc, pumice stone and kieselguhr were strongly coloured. With acid dyes, these also remained colourless. Experiments with naturally occurring silicates showed that the acid silicates were strongly coloured by magenta and methylene-blue, but that the neutral or basic silicates remained colourless or almost so. Augite and petalite form exceptions to this rule.

As a solution of phenolphthalein in water made just alkaline with ammonia and a solution of copper hydroxide in insufficient ammonia to completely dissolve it are decolorised by starch or kaolin, these substances must act as weak acids towards bases.

As in the case of starch, when kaolin is treated with a basic dye, the hydrochloric acid is quantitatively separated from the dye-base and neutralised by the mineral base; in the dyeing of wool, the acid is probably neutralised by mineral constituents or by an amine from the fibres. Kaolin is dyed red, in the same manner as is wool, when warmed with the carbinol base of triaminotriphenylmethane (Jacquemin).

By a series of experiments, it is shown that the amount of the dye (magenta, methylene-blue, crystal-violet) taken up by kaolin does not vary with the temperature or concentration of the bath, but diminishes on addition of an excess of acid.

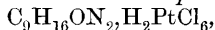
The author concludes that the process of dyeing starch, kaolin, or wool takes place by a chemical reaction and not a physical action.

G. Y.

Action of Methylamine and of Dimethylamine on Furfuraldehyde. FRANZ M. LITERSCHIED (*Annalen*, 1904, **335**, 368—378. Compare Schwabbauer, *Abstr.*, 1902, i, 230).—Furfurylidenemethylamine, formed by the action of methylamine on furfuraldehyde, without cooling, yields a *hydrochloride*, $C_4H_3O \cdot CH:NMe, HCl$, which crystallises in leaflets; the *platinichloride*, $(C_4H_3ON)_2, H_2PtCl_6, H_2O$, crystallises in prisms, decomposes at about 128° , and loses H_2O at 100° ; the *aurichloride*, $C_4H_3ON, HAuCl_4$, forms a microscopic, crystalline precipitate and melts at about 130° ; the *methiodide*, C_4H_3ON, MeI , is formed as a yellow product.

The action of methylamine on furfuraldehyde, when cooled by ice, leads to the formation of a *substance* which yields an unstable *platinichloride*, $[C_4OH_3 \cdot CH(OH) \cdot NHMe]_2, H_2PtCl_6 (?)$; it decomposes on drying into furfuraldehyde and methylamine platinichloride.

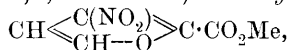
Furfurylidenetetramethyldiamine, $C_4H_3O \cdot CH(NMe_2)_2$, formed by the action of dimethylamine on furfuraldehyde, without cooling, is a liquid with a strongly ammoniacal odour. The *platinichloride*,



is a yellow, crystalline precipitate and decomposes on recrystallisation; the *dimethiodide*, $C_9H_{16}ON_2, 2MeI$, forms a yellow, crystalline precipitate and yields an *aurichloride*, $C_4H_3O \cdot CH(NMe_2)_2, 2AuCl_4$, which is a yellow, prismatic, crystalline powder and melts at 174° ; the *platinichloride* of the dimethochloride crystallises in small rosettes.

G. Y.

Nitration of Methyl Pyromucate. Nitropyromucic Acid. R. MARQUIS (*Bull. Soc. chim.*, 1904, [iii], **31**, 1277—1282. Compare Abstr., 1902, i, 388, 483; 1903, i, 49 and 644).—*Methyl nitropyromucate*,



prepared by esterifying nitropyromucic acid (Abstr., 1903, i, 49) or by nitrating methyl pyromucate, crystallises in pale yellow lamellæ and melts at 78.5°. *Nitropyromucyl chloride* crystallises in greasy lamellæ and melts at 38°; the *amide*, obtained by the action of dry ammonia on the chloride dissolved in ether, forms silky, white needles and melts at 161°; the *anilide*, similarly prepared, crystallises in lemon-yellow needles and melts at 180°, the *p-toluidide* forms yellow prisms and melts at 162°. Nitropyromucic acid is completely decomposed by the usual oxidising agents, but the ethyl ester is oxidised by sodium dioxide forming fumaric and nitrous acids. T. A. H.

isoPyromucic Acid. G. CHAVANNE (*Ann. Chim. Phys.*, 1904, [viii], **3**, 507—574).—In addition to the derivatives of *isopyromucic acid* described in previous papers (compare Abstr., 1901, i, 649; 1902, i, 637, 690; 1903, i, 270; 1904, i, 82), the original contains an account of the preparation and properties of the following derivatives: *iodoisopyromucic acid*, $\text{C}_5\text{H}_3\text{O}_3\text{I}$, prepared by the action of iodine and mercuric oxide on *isopyromucic acid*, crystallises in large, short prisms melting at 150—151° and is soluble in alcohol; by the action of water in sealed tubes at 175° on *isopyromucic acid*, two *compounds* having the composition $\text{C}_9\text{H}_6\text{O}_3$ are obtained, melting at 186° and 155—160° respectively; the *compound* $\text{C}_5\text{H}_4\text{O}_4\text{Br}_2$, obtained by the action of bromine water at 0° on *bromoisopyromucic acid*, is sparingly soluble in cold water, soluble in alcohol, acetone, or boiling ether, chloroform or benzene; the *compound* $\text{C}_4\text{H}_2\text{O}_2\text{Br}_2$ (probably *dibromomaleic dialdehyde*, $\text{CHO} \cdot \text{CBr} : \text{CBr} \cdot \text{CHO}$), obtained by the action of excess of bromine on *isopyromucic acid* at 60°, boils at 132° under 15 mm. pressure, forms large crystals melting at 34°, and is converted quantitatively into mucobromic acid, $\text{CHO} \cdot \text{CBr} : \text{CBr} \cdot \text{CO}_2\text{H}$, on warming with bromine water. The author suggests the following constitutional formula for *isopyromucic acid*, $\text{CH} \begin{array}{c} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \cdot \text{CO} \end{array} \text{O}$.

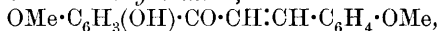
M. A. W.

Compounds of Dimethylpyrone with Trichloroacetic Acid. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1088—1091).—Dimethylpyrone forms two compounds with trichloroacetic acid: (1) the *normal salt*, $\text{C}_7\text{H}_8\text{O}_2 \cdot \text{CCl}_3 \cdot \text{CO}_2\text{H}$, which melts at 45½—46½°, and (2) the *acid salt*, $\text{C}_7\text{H}_8\text{O}_2 \cdot 2\text{CCl}_3 \cdot \text{CO}_2\text{H}$, which melts at 66½—67½°. T. H. P.

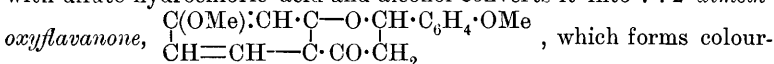
7:2-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and A. VON SZLAGIER (*Ber.*, 1904, **37**, 4155—4158. Compare Abstr., 1904, i, 441, 442, 608).—The conclusion of Kostanecki and Katschalowsky (Abstr., 1904, i, 608) with reference to the tinctorial properties of the dihydroxyflavonols is found to be erroneous, owing to the widely

differing solubilities of the isomerides. When tested under similar conditions, the less soluble compounds being employed in the form of paste, the 6:2', 6:3', 6:4', 7:2', 7:3', and 7:4'-dihydroxyflavonols are all found to dye cotton mordanted with alumina. The *anchi*-position of the hydroxyl groups is therefore without influence on the tinctorial properties.

2'-Hydroxy-4':2-dimethoxychalkone,

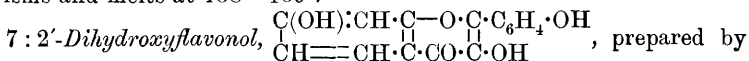


prepared by condensing salicylaldehyde methyl ether with paeonol, crystallises from alcohol in deep yellow needles melting at 94° and dissolves in concentrated sulphuric acid to an orange solution. Boiling with dilute hydrochloric acid and alcohol converts it into 7:2'-dimethoxyflavanone,



less, prismatic needles melting at 102° and dissolving in concentrated sulphuric acid or alcoholic sodium hydroxide to yellow solutions. Its 3-isonitroso-derivative, prepared by the action of amyl nitrite and hydrochloric acid, forms white tablets and melts and decomposes at 195°.

7:2'-Dimethoxyflavonol, prepared by the hydrolysis of the isonitroso-compound, forms bright yellow, striated tablets and melts at 203°. It forms a sparingly soluble *sodium* salt and dissolves in concentrated sulphuric acid to a yellow solution which shows a bright blue fluorescence after dilution. The *acetyl* derivative forms short, glistening prisms and melts at 138—139°.



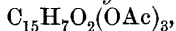
boiling the dimethoxy-compound with concentrated hydriodic acid, forms yellowish-white needles melting at 271° and dissolves in dilute sodium hydroxide to a pale yellow solution with strong green fluorescence. The solution in concentrated sulphuric acid is pale yellow, and shows a strong blue fluorescence on dilution. C. H. D.

7:3'-Dihydroxyflavonol. STANISLAUS VON KOSTANECKI and A. WIDMER (*Ber.*, 1904, **37**, 4159—4161).—2'-Hydroxy-4':3-dimethoxychalkone, prepared from *m*-methoxybenzaldehyde and paeonol, crystallises from alcohol in yellow prisms and melts at 80—81°; its *acetyl* derivative forms pale yellow leaflets melting at 70—71°. Warming with dilute sulphuric acid and alcohol converts it into 7:3'-dimethoxyflavanone, crystallising in white needles melting at 104°. The 3-isonitroso-derivative forms small, pale yellow prisms and melts and decomposes at 160°.

7:3'-Dimethoxyflavonol crystallises from alcohol in almost colourless needles and melts at 170°. It forms a yellow, sparingly soluble *sodium* salt, and dissolves in concentrated sulphuric acid to a pale yellow solution with green fluorescence. The *acetyl* derivative forms colourless needles melting at 165°.

7:3'-Dihydroxyflavonol forms white needles melting at 298—300°, and dissolves in dilute sodium hydroxide to a bright yellow solution

with slight green fluorescence. *Acetyl-7 : 3'-diacetoxyflavonol*,



forms white needles and melts at 169° .

C. H. D.

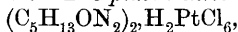
7 : 4'-Dihydroxyflavonol. K. JUPPEN and STANISLAUS VON KOSTANECKI (*Ber.*, 1904, **37**, 4161—4163).—7 : 4'-*Dimethoxyflavanone*, obtained from 2'-hydroxy-4' : 4-dimethoxychalkone (Kostanecki and Osius, *Abstr.*, 1899, i, 370), forms colourless needles melting at $94-95^\circ$. Its 3-isonitroso-derivative crystallises from benzene in groups of small prisms and melts and decomposes at 170° .

7 : 4'-*Dimethoxyflavonol* forms bright yellow crystals, melts at $196-197^\circ$, and dissolves sparingly in alcohol. Its solution in concentrated sulphuric acid is yellow and shows an intense green fluorescence. The *acetyl* derivative forms colourless tablets melting at $193-194^\circ$.

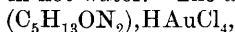
7 : 4'-*Dihydroxyflavonol* crystallises from dilute alcohol in bright yellow needles melting at 310° . It dissolves in dilute sodium hydroxide to a yellow solution with green fluorescence. Its *triacetyl* derivative forms white needles melting at 153° .

C. H. D.

[**New Alkaloid in**] **Earth-nut.** W. MOOSER (*Landw. Versuchs-Stat.*, 1904, **60**, 321—346).—Earth-nut meal contains, in addition to the bases choline and betaine, isolated by Schulze, an alkaloid *arachine*, $\text{C}_5\text{H}_{14}\text{ON}_2$. It was obtained as a yellowish-green syrup, rather readily soluble in water and alcohol, less so in chloroform, and insoluble in light petroleum or ether. The *platinichloride*,



is an orange-coloured, crystalline substance melting at 216° , soluble in cold water and insoluble in hot water. The *aurichloride*,



forms lemon-coloured, strongly refractive crystals. Both double salts crystallise in a variety of forms.

Subcutaneous injection of arachine hydrochloride immediately produced somnolence with frogs and rabbits, and partial paralysis. In the case of frogs, cutting off the toes produced no movement. The effect of the poison passed off the next day.

A number of samples of earth-nut meal were examined and all were found to contain the alkaloid.

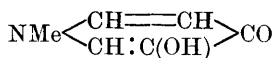
N. H. J. M.

Quaternary Ammonium Compounds of the Alkaloids. MAX SCHOLTZ and K. BODE (*Arch. Pharm.*, 1904, **242**, 568—574).—Whereas 1-alkyl derivatives of coniine and of conhydrine yield two isomeric additive products with an alkyl haloid containing a different alkyl group (*Abstr.*, 1904, i, 1044), the alkaloids detailed below yield only one additive product in each case; the numbers quoted are melting points.

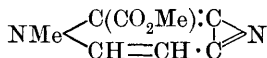
Brucine with *benzyl bromide*. *Strychnine* with *benzyl bromide*; with *methyl iodoacetate* (240°). *Cinchonine* with *methyl iodoacetate* (200°). *Nicotine* with *benzyl iodide* (2 mols.) ($214-215^\circ$). *Tropine* with *methyl iodoacetate* (212°); with *benzyl iodide* (236°). *Atropine* with *benzyl bromide* (215°).

C. F. B.

Constitution of Ricinine. LÉON MAQUENNE and LOUIS PHILIPPE (*Compt. rend.*, 1904, 139, 840—843. Compare Abstr., 1904, i, 339).—The hydroxymethylpyridone obtained by the successive action of potassium hydroxide and fuming hydrochloric acid on ricinine has feebly basic properties, forming a crystalline hydrochloride, phosphate, and platinichloride, and it behaves as a monobasic acid towards phenolphthalein. It readily yields substituted derivatives by the action of bromine, and the compounds $C_6H_5O_2NBr$, $C_6H_5O_2NBr_2$, and $C_6H_3O_2NBr_4$ are crystalline, soluble in alcohol, and much more strongly acidic than the original compound. The *nitro*-derivative, $C_6H_4O_2N(NO_2)$, crystallises in yellow needles and forms well-defined salts; the *calcium* salt, $(C_6H_5O_4N_2)_2Ca \cdot 5H_2O$, crystallises in thin needles and the *ammonium* and *potassium* salts are also crystalline. Phosphorus pentachloride at 160° reacts with hydroxymethylpyridone to form two chlorinated derivatives, of which the one formed in the larger quantity is a *dichloropyridine*, $C_5H_3NCl_2$, boiling at 98° under 18 mm. pressure and reduced by hydrogen iodide and red phosphorus at 170° to pyridine. Hydroxymethylpyridone and ricinine are therefore derivatives of a hydroxypyridine in which the methyl group is attached to the nitrogen, as represented in the following formulæ:



Hydroxymethylpyridone.



Ricinine.

M. A. W.

The Development of the Chemistry of Pyrrole in the Last Twenty-five Years. GIACOMO L. CIAMICIAN (*Ber.*, 1904, 37, 4200—4255).—A lecture delivered before the German Chemical Society.

C. H. D.

2:6-Tetramethylpiperidine. ANTOINE P. N. FRANCHIMONT and H. FRIEDMANN (*Proc. k. Akad. Wetensch. Amsterdam*, 1904, 7, 270—271).—2:2:6:6-Tetramethylpiperidine, prepared by the reduction of 3-bromo-2:2:6:6-tetramethylpiperidine by the zinc-copper couple, has the sp. gr. 0.8367 and boils at 155.5 — 156.5° under 760 mm. pressure. With water, it forms a crystalline compound which melts at 28° . The *hydrochloride* and *hydrobromide* sublime, the *hydrogen sulphate* melts at 174° and the *normal sulphate* at 270° . The base reacts very slowly with acid chlorides. Its *methylurethane* has the sp. gr. 0.9848 and boils at 227° under 760 mm. pressure; its *benzoyl* derivative melts at 41 — 42° and its *picrate* at 225° .

A. McK.

o-Thymotinpiperidide. HERMANN HILDEBRANDT (*Ber.*, 1904, 37, 4456—4458. Compare Abstr., 1900, ii, 676; Kobek, Abstr., 1884, 56; Manasse, Abstr., 1894, i, 577; 1903, i, 28).—On administering thymotic alcohol to rabbits and treating their urine with hydrochloric acid and sodium hypochlorite, there is obtained *dichlorothymotinglycuronic anhydride*, $C_{17}H_{18}O_8Cl_2$, which melts at 80° . The *base*, $C_{17}H_{25}ON$, obtained by warming thymotic alcohol with piperidine and formaldehyde, melts at 140° , and when administered to rabbits appears

in the urine as the same glycuronic acid compound (m. p. 192°) as is obtained from *p*-thymotinpiperidide. This, on hydrolysis with 6—8 per cent. sulphuric acid, yields *o*-thymotinpiperidide, $C_{16}H_{25}ON$, which melts at 141° , gives the thymol reaction when boiled with glacial acetic and sulphuric acids, and is converted into a glycuronic acid compound when administered to rabbits. G. Y.

2-Methyl-dihydroindole. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1904, **37**, 4581—4584).—Benzoylmethyl-dihydroindole, when heated to 150 — 160° with phosphorus pentachloride, is converted into the *imide-chloride*, $CPhCl:N \cdot C_6H_4 \cdot CH_2 \cdot CHMeCl$, of which the benzoyl compound, obtained on hydrolysis, *benzoyl-o*- β -chloropropylanilide, $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot CHClMe$, was isolated. This crystallises in long, colourless needles melting at 130 — 131° .

The *benzenesulphonyl* derivative, $C_6H_4 \langle \overset{CH_2}{\underset{N(SO_2Ph)}{\text{---}}} \rangle CHMe$, is well suited to characterise methyl-dihydroindole; it separates in glassy, glistening crystals melting at 90° . E. F. A.

Constitution of Ethyl 6:8-Dinitrotetrahydroquinoline-1-carboxylate. G. C. A. VAN DORP (*Rec. Trav. Chim.*, 1904, **23**, 301—323).—*Ethyl tetrahydroquinoline-1-carboxylate*, prepared by the action of ethyl chlorocarbonate on tetrahydroquinoline, is a colourless, highly refractive liquid, which solidifies when cooled and then melts at 27° and boils at 168.5° under 12 mm. or at 181° under 25 mm. pressure. When treated in acetic acid solution with anhydrous nitric acid, it furnishes *ethyl 6(?)-nitrotetrahydroquinoline-1-carboxylate*; this crystallises from alcohol in colourless needles, melts at 78.5° , and by sodium ethoxide is converted into the corresponding nitrotetrahydroquinoline, which melts at 159° (compare Stoermer and Dragendorff, *Abstr.*, 1899, i, 45). *Ethyl 6:8-dinitrotetrahydroquinoline-1-carboxylate*, prepared by adding the ester to anhydrous nitric acid cooled to -5° , crystallises from alcohol in small, faintly yellow plates, melts at 97.5° , and is not acted on by aqueous solutions of potassium hydroxide, but, with sodium ethoxide dissolved in cold alcohol or when heated at 90° with dilute sulphuric acid, yields the corresponding dinitrotetrahydroquinoline, which melts at 164° (compare Simon Thomas, *Abstr.*, 1892, 725), and on oxidation furnishes 6:8-dinitroquinoline.

When ethyl 6:8-dinitrotetrahydroquinoline-1-carboxylate is oxidised with chromic acid, β -3:5-dinitro-2-aminocarbethoxyphenylpropionic acid and 3:5-dinitro-2-aminobenzoic acid (m. p. 268°) are produced; the former crystallises in colourless needles, melts and decomposes at 211° , dissolves in alcohol and mineral acids, and is reprecipitated on addition of water. When boiled with an aqueous solution of potassium hydroxide, it resinifies and gives off ammonia. The *ethyl* ester crystallises in needles from a mixture of acetone and water or from alcohol and melts at 134.5° . The free acid, when dissolved in alcohol and heated with sulphuric acid, yields 6:8-dinitro-2-ketotetrahydroquinoline, which is crystalline and melts at 177° ; when boiled with aqueous potash, this furnishes Zwenger's dinitromelilotic acid, β -3:5-dinitro-2-hydroxyphenylpropionic acid.

Methyl tetrahydroquinoline-1-carboxylate forms yellow crystals, melts at 33°, and boils at 172° under 13 mm. pressure; the corresponding 6:8-dinitro-derivative melts at 180·5—181°. 1-Phenylsulphone-tetrahydroquinoline melts at 64·5—65°, and its 6:8-dinitro-derivative crystallises from benzene and melts at 215° (compare Schotten and Schlömann, Abstr., 1892, 351).

Methyl 2-methyltetrahydroquinoline-1-carboxylate, prepared by the action of methyl chlorocarbonate on quinaldine, melts at 42·5° and boils at 239—240°.

1-Phenylsulphone-2-methyltetrahydroquinoline forms colourless crystals from alcohol and melts at 109·5° to 110°. T. A. H.

Derivatives of Chrysene. CARL GRAEBE (*Annalen*, 1904, 335, 122—138. Compare Abstr., 1900, i, 505; this vol., i, 60).—Chrysodiphen-2'-amic acid, $\text{CO}_2\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, which melts at 220°, does not form an ester when treated with methyl alcohol and hydrogen chloride; when heated with concentrated hydrochloric acid at 150°, it is hydrolysed to chrysodiphenic acid. The isomeric amic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is not found to melt at 275°; it is not hydrolysed by hydrochloric acid at 150°; with methyl alcohol and hydrogen chloride, it forms a *methyl* ester which melts at 170°.

α-Naphthaphenanthrindone, $\begin{array}{c} \text{C}_{10}\text{H}_6\cdot\text{NH} \\ | \\ \text{C}_6\text{H}_4-\text{CO} \end{array}$, formed from chrysodiphen-1-amic acid by the action of sodium hypochlorite in aqueous sodium hydroxide solution, melts at 332·5°, sublimes, and dissolves in concentrated sulphuric acid to a colourless solution with slight blue fluorescence. When heated with zinc dust, it yields a *naphthaphenanthrindine*, $\begin{array}{c} \text{C}_{10}\text{H}_6\cdot\text{N} \\ | \\ \text{C}_6\text{H}_4-\text{CH} \end{array}$, which crystallises in colourless leaflets, melts at 135·5° (corr.), and dissolves in concentrated sulphuric acid to a colourless solution with a blue fluorescence; the *hydrochloride*, $\text{C}_{17}\text{H}_{11}\text{N}\cdot\text{HCl}\cdot\text{H}_2\text{O}$, melts and decomposes at 235°; the *aurichloride* melts at 218°; the *mercurichloride* melts at 258°; the *picrate* melts and decomposes at 256°.

β-Naphthaphenanthrindone, $\begin{array}{c} \text{C}_{10}\text{H}_6\cdot\text{CO} \\ | \\ \text{C}_6\text{H}_4-\text{NH} \end{array}$, obtained from chrysodiphen-2'-amic acid, melts at 338°. *β-Naphthaphenanthrindine*, $\begin{array}{c} \text{C}_{10}\text{H}_6\cdot\text{CH} \\ | \\ \text{C}_6\text{H}_4-\text{N} \end{array}$, crystallises in colourless leaflets and melts at 182°; the *hydrochloride*, $\text{C}_{17}\text{H}_{11}\text{N}\cdot\text{HCl}$, melts at 220°.

β-Chrysenic acid (2-phenylnaphthalene-1-carboxylic acid), $\text{C}_{10}\text{H}_6\cdot\text{Ph}\cdot\text{CO}_2\text{H}$ (Graebe, Abstr., 1900, i, 296), yields chrysoketone when treated with concentrated sulphuric acid; the *silver* salt, $\text{C}_{17}\text{H}_{11}\text{O}_2\text{Ag}$, is insoluble in water; the *methyl* ester, $\text{C}_{18}\text{H}_{14}\text{O}_2$, obtained by the action of methyl iodide on the silver salt, melts at 75° and is only very slightly hydrolysed by boiling alcoholic sodium hydroxide; no amide is formed when the acid is treated with phosphorus pentachloride and ammonia.

The *oxime*, $\begin{array}{c} \text{C}_{10}\text{H}_6 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{C}\cdot\text{N}\cdot\text{OH}$, prepared from specimens of chrysoketone obtained by different processes, melts and decomposes at 202°.

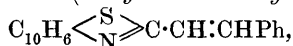
Chrysofluorene, $\text{C}_{10}\text{H}_6 > \text{C}_6\text{H}_4 > \text{CH}_2$, is best prepared from the ketone in small quantities by heating with zinc dust, and in larger quantities by boiling with 50 per cent. hydriodic acid and red phosphorus. It boils at 413° , is easily soluble in hot benzene or chloroform, and is oxidised to chrysoketone by sodium dichromate in glacial acetic acid solution; the picrate, $\text{C}_{17}\text{H}_{12} \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms orange-red crystals and melts at 127.5° .

Dinaphthylenediphenylene-ethylene, $\text{C}_{10}\text{H}_6 > \text{C}:\text{C} < \text{C}_{10}\text{H}_6$, formed when chrysofluorene is heated with lead oxide at $320\text{--}330^\circ$ or distilled with lead oxide under reduced pressure, melts at $180\text{--}190^\circ$, forms intensely red solutions, and yields, with bromine, a colourless *additive* compound; a colourless *hydrocarbon* (*dinaphthylenediphenylene-ethane*?), which melts at 257° , is formed along with the ethylene by the action of lead oxide on chrysofluorene.

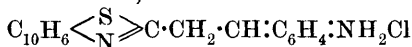
G. Y.

Chromophorous Groups. II. Methineammonium Dyes. HANS RUPE and GEORG L. M. SCHWARZ (*Zeit. Farb. Text.-Ind.*, 1904, 397—402).—The following thiazoles are analogous to the iminazole-dyes described in a previous paper (Rupe and Porai-Koschitz, *Abstr.*, 1904, i, 107).

2-Styryl-β-naphthathiazole (*benzylidene-2-methyl-β-naphthathiazole*),



prepared by heating 2-methyl-β-naphthathiazole with benzaldehyde and zinc chloride at $160\text{--}170^\circ$, crystallises from glacial acetic acid in white needles and melts at $148\text{--}149^\circ$. 2-*o*-Chlorostyryl-β-naphthathiazole crystallises from pyridine and melts at 158° . 2-*o*-Nitrostyryl-β-naphthathiazole crystallises from glacial acetic acid or from pyridine in yellow needles, melts at 183° , and on reduction in alcoholic solution with stannous chloride and hydrochloric acid gives 2-*o*-aminostyryl-β-naphthathiazole, which crystallises from pyridine and melts at 225° ; the *hydrochloride* of this base dyes mordanted cotton and probably has the quinonoid structure,



(compare *loc. cit.*). 2-*o*-Acetylaminostyryl-β-naphthathiazole crystallises from alcohol and melts at 249° .

2-*m*-Nitrostyryl-β-naphthathiazole, prepared by means of *m*-nitrobenzaldehyde, crystallises from glacial acetic acid in yellow needles and melts at 200° . 2-*m*-Aminostyryl-β-naphthathiazole forms yellow leaflets, melts at 194° , is without tinctorial properties, and therefore probably has the structure $\text{C}_{10}\text{H}_6 < \begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix} > \text{C}:\text{CH}:\text{CH}:\text{C}_6\text{H}_4:\text{NH}_2\text{HCl}$; its *acetyl* derivative forms yellow needles and melts at 215° . 2-*p*-Nitrostyryl-β-naphthathiazole forms orange-yellow needles and melts at 228° . The *p*-amino-compound is a yellow, crystalline powder melting at 245° ; its *acetyl* derivative crystallises from glacial acetic acid in white needles and melts at 223° .

2-Dimethyl-*p*-aminostyryl-β-naphthathiazole, prepared by means of

p-aminobenzaldehyde, forms bright yellow crystals, melts at 212° , and gives a *dihydrochloride* which is hydrolysed by water to form the base; it has marked tinctorial properties.

2-*o*-Hydroxystyryl- β -naphthathiazole, obtained from salicylaldehyde, crystallises from pyridine and melts at 249° . 2-*p*-Hydroxystyryl- β -naphthathiazole melts at 271° and gives an *acetyl* derivative melting at 159° .

The following compounds were prepared from 2-methyl- α -naphthathiazole. 2-*o*-Chlorostyryl- α -naphthathiazole crystallises from pyridine in yellow needles and melts at 144° . 2-*o*-Nitrostyryl- α -naphthathiazole is similar and melts at 168° . 2-*o*-Aminostyryl- α -naphthathiazole crystallises from pyridine or amyl alcohol in yellow leaflets and melts at 185° ; its *acetyl* derivative crystallises from alcohol in yellow needles melting at 238° .

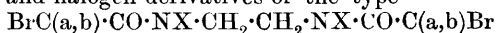
2-*m*-Nitrostyryl- α -naphthathiazole melts at 190° ; 2-*m*-aminostyryl- α -naphthathiazole forms yellow needles, melts at 152° , and gives salts which are colourless; its *acetyl* derivative melts at 242° .

2-*p*-Nitrostyryl- α -naphthathiazole forms lustrous needles and melts at 226° . 2-*p*-Aminostyryl- α -naphthathiazole crystallises in yellow needles and forms a deep red *hydrochloride*; the *acetyl* derivative melts at 218° .

W. A. D.

Formation of Chains. LX. Reactions of the Benzyanilide of α -Bromopropionic Acid and of Di- α -monobromopropionyl-diphenylethylenediamine. CARL A. BISCHOFF and, in part, with FRÖHLICH, JACKOWLEW, KISSIN, MAZARAKI, MILEWSKI, and PILDON (*Ber.*, 1904, 37, 4341—4350. Compare Abstr., 1901, i, 524—528).—The condensation of the benzanilide of α -bromopropionic acid with the sodium derivatives of phenol, *o*-cresol, thymol, and carvacrol has been studied in benzene, toluene, and xylene solutions in order to determine whether the presence of ortho-methyl or isopropyl groups had a retarding or disturbing effect. No such effect could be detected as the yields in the different cases were much the same. In all cases the reaction was normal and no acrylic acid derivatives were obtained. *o*-Tolylxypropionylbenzyaniline, $C_6H_4Me \cdot O \cdot CHMe \cdot CO \cdot NPh \cdot CH_2Ph$, crystallises in large, rhombic plates melting at 60 — 61° . The corresponding *thymo*xy-compound forms colourless triclinic plates melting at 52° and readily soluble in all solvents, and the *carvacro*xy-compound crystallises in compact, monoclinic prisms melting at 60 — 61° .

The reactions between the sodium derivatives of phenol and of α - and β -naphthols and halogen derivatives of the type

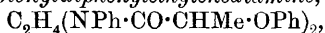


have been studied. The reaction is termed normal when the product is of the type $Z \cdot O \cdot C(a,b) \cdot CO \cdot NX \cdot CH_2 \cdot CH_2 \cdot NX \cdot CO \cdot C(a,b) \cdot O \cdot Z$ (where $Z = C_6H_5$ or $C_{10}H_7$), and abnormal when the products are an unsaturated compound, $C_nH_{2n-1} \cdot CO \cdot NX \cdot CH_2 \cdot CH_2 \cdot NX \cdot CO \cdot C_nH_{2n-1}$, and a phenol, $2Z \cdot OH$. The extent to which the abnormal reaction proceeded was determined by extracting the phenol with sodium hydroxide and estimating the free phenol.

The reaction between di- α -bromopropionyl-diphenylethylenediamine (compare Abstr., 1893, i, 78) and the sodium derivatives of phenol,

o-cresol, α -naphthol, β -naphthol, ethyl salicylate, and ethyl malonate in benzene, toluene, or xylene solutions is of the normal type and is practically complete after boiling for some 20 hours.

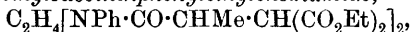
Diphenoxy- α -dipropionyldiphenylethylenediamine,



crystallises in glistening needles sparingly soluble in hot light petroleum. The corresponding *di-o-tolyl*oxy- and *di-p-tolyl*oxy-compounds have not been obtained in a crystalline form. The *di- α -naphthoxy*-derivative, $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7)_2$, crystallises from alcohol in colourless needles melting at 155° and is only sparingly soluble in ether, light petroleum, or cold alcohol. The isomeric *β -naphthoxy*-derivative melts at $90\text{--}94^\circ$.

The compound obtained from the sodium derivative of ethyl salicylate, $\text{C}_2\text{H}_4(\text{NPh}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et})_2$, crystallises from methyl alcohol in compact needles melting at 141° and is insoluble in ether or light petroleum. When hydrolysed with alcoholic potash and acidified, the corresponding *acid*, $\text{C}_{34}\text{H}_{32}\text{O}_8\text{N}_2$, is obtained. This crystallises from glacial acetic acid in colourless prisms melting at 276° and is insoluble in most solvents.

Dicarbethoxymethylsuccindiphenylethylenediamide,



obtained from ethyl sodiomalonate, crystallises in colourless plates, melts at 166° , and is only sparingly soluble in ether or light petroleum.

J. J. S.

Formation of Chains. LXI. Reactions with Di- α -propionyl-ditolylethylenediamine. CARL A. BISCHOFF (MATZ and VON WODZINSKY) (*Ber.*, 1904, **37**, 4350—4355. Compare preceding abstract).—The reaction between α -bromopropionyl-di-*p*-tolylethylenediamine and the sodium derivatives of phenol α - and β -naphthols is perfectly normal, and, after 20 hours, some 90—99 per cent. of sodium bromide is formed. The *diphenoxy*-derivative, $\text{C}_2\text{H}_4[\text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OPh}]_2$, forms colourless crystals melting at 130° ; an *isomeride*, melting at $101\text{--}102^\circ$, has also been obtained. The *di- α -naphthoxy*-derivative melts at $50\text{--}52^\circ$, and the reaction is practically normal, only some 4 per cent. of free naphthol being formed. The *di- β -naphthoxy*-compound crystallises from dilute alcohol in needles melting and decomposing at $90\text{--}91^\circ$, and seems to consist of a mixture of two substances melting respectively at 89° and $92\text{--}95^\circ$.

α -Bromopropionyl-di-*o*-tolylethylenediamine condenses with the same sodium salts, but the reaction proceeds more slowly owing to the presence of the *o*-methyl groups, and is to a certain extent abnormal. The *diphenoxy*-derivative crystallises in microscopic, six-sided prisms melting at $137\text{--}138^\circ$. The *di- α -naphthoxy*-compound melts at $153\text{--}154^\circ$ and the *di- β -naphthoxy*-derivative at $195\text{--}196^\circ$. The yields of free phenols were: phenol 4, α -naphthol 12, and β -naphthol 8 per cent.

J. J. S.

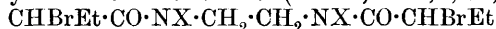
Formation of Chains. LXII. Reactions of Di- α -bromopropionyl-dinaphthylethylenediamine. CARL A. BISCHOFF (*Ber.*, 1904, **37**, 4356—4362. Compare preceding abstracts).—[With SCHTSCHEGOLEW.]—Di- α -bromopropionyl-di- α -naphthylethylenediamine (*Abstr.*, 1893,

i, 98) condenses with the sodium derivatives of phenols, but the reaction is to a certain extent abnormal. The *diphenoxy*-derivative appears to exist in two isomeric forms, the one sintering at 218° and melting at 223°, and the other melting at 192°. The yield of free phenol was 12 per cent. The *di-α-naphthoxy*-derivative has only been obtained in the form of an amorphous mass melting at about 80°. The yield of *α*-naphthol was 13 per cent. The *di-β-naphthoxy*-derivative crystallises in four-sided plates and melts at 204°. The yield of free naphthol was about 10 per cent.

[With SOLOWEITSCHIK.]—The * corresponding reactions with the isomeric *di-α-bromopropionyl-di-β-naphthylethylenediamine* have been studied. *Diphenoxy-α-propionyl-di-β-naphthylethylenediamine*, after recrystallisation from acetic acid and ethyl acetate, forms microscopic, rhombohedral crystals sintering at 185° and melting at 192—193°. The corresponding *di-α-naphthoxy*-derivative has only been obtained in an amorphous state, but the isomeric *di-β-naphthoxy*-compound crystallises in glistening needles melting at 182°. It is but sparingly soluble in ether, light petroleum, or alcohol, but dissolves readily in chloroform. The yields of free phenols were respectively 4, 7, and 4 per cent., indicating that the reactions were practically normal. Pure *di-α-naphthylethylenediamine* melts at 133—134° (compare Abstr., 1890, 1333).

J. J. S.

Formation of Chains. LXIII and LXIV. Reactions of Di-*α*-monobromobutyryldiarylethylenediamines and of Di-*α*-monobromo*isobutyryldiarylethylenediamines*. CARL A. BISCHOFF and, in part, with VON BERENT, FRÄNKEL, JASINSKY, LANIN, MIRONENKO, PESCHUDOW, STEIN, TOBILEWITSCH, TROZKI, WINOKUROW, and WULFFIUS (*Ber.*, 1904, 37, 4548—4556, 4556—4570. Compare Abstr., 1901, i, 524—528, and preceding abstracts).—The reactions between the following ethylenediamine derivatives (Abstr., 1893, i, 78, 98),



and $\text{CBrMe}_2 \cdot \text{CO} \cdot \text{NX} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NX} \cdot \text{CO} \cdot \text{CBrMe}_2$ (where X = phenyl, *o*-tolyl, *p*-tolyl, *α*-naphthyl, or *β*-naphthyl), and the sodium derivatives of phenol *α*- and *β*-naphthols have been studied.

The relative reactivities of the compounds with sodium phenoxide in benzene solution are shown in the following table, where the numbers represent the per cent. of sodium bromide formed after one hour.

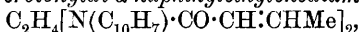
X	Propionyl.	Butyryl.	<i>iso</i> Butyryl.
Phenyl	54	44	29
<i>p</i> -Tolyl	49	43	27
<i>β</i> -Naphthyl.....	55	42	22
<i>α</i> -Naphthyl.....	43	42	19
<i>o</i> -Tolyl.....	40	39.5	25

The reactions with the butyryl derivatives in all cases led to the formation of a considerable amount of the abnormal products, namely, unsaturated compound and free phenol. This abnormality was the

most pronounced (some 32—50 per cent.) when $X = o$ -tolyl or α -naphthyl with both butyl and isobutyl compounds. In nearly all cases, over 90 per cent. of the theoretical amount of sodium bromide was obtained by heating for a sufficient length of time.

Di- α -crotonyldiphenylethylenediamine, $C_2H_4(NPh \cdot CO \cdot CH : CHMe)_2$, crystallises from dilute alcohol in glistening needles melting at 174 — 176° , and only sparingly soluble in light petroleum or ether. It has been obtained by the condensation of di- α -bromobutyryldiphenylethylenediamine with the sodium derivatives of phenol and of α - and β -naphthol; although considerable amounts of the normal products were also formed, they could not be obtained in a crystalline state.

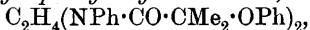
Di- α -crotonyldi- o -tolylethylenediamine crystallises in colourless needles and melts at 211° , and the isomeric *di- p -tolyldiamine* melts at 183° . The *di- α -crotonyldi- α -naphthylethylenediamine*,



also crystallises in colourless needles, melts at 218° , and is sparingly soluble in methyl alcohol, ether, or light petroleum. The normal condensation products, *di-phenoxybutyryldi- α -naphthylethylenediamine* (melting at 54°) and the corresponding *di- α -naphthoxy-* (melting at 58 — 60°) and *di- β -naphthoxy-* (melting at 58 — 60°) derivatives have been isolated.

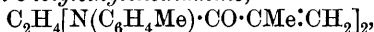
Di- α -crotonyldi- β -naphthylethylenediamine melts at 208° and dissolves readily in chloroform or benzene. The normal condensation products, *di-phenoxybutyryldi- β -naphthylethylenediamine* (melting at 55 — 57°) and the corresponding *di- α -naphthoxy-* (melting at 65 — 67°) and *di- β -naphthoxy-* derivatives (melting at 59 — 60°), have only been obtained in an amorphous state.

Di-phenoxyisobutyryldiphenylethylenediamine,



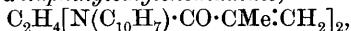
crystallises from glacial acetic acid in glistening plates melting at 200 — 203° . The *di- α -naphthoxy-* derivative was only obtained as a resin, and the *di- β -naphthoxy-* compound as glistening needles melting at 182° .

Di-methylacryldi- o -tolylethylenediamine,



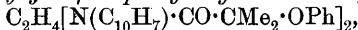
crystallises in glistening needles melting at 131° and readily soluble in acetone, benzene, or chloroform. *Di- β -naphthoxyisobutyryldi- o -tolylethylenediamine* melts at 206° . *Di-phenoxyisobutyryldi- p -tolylethylenediamine* crystallises in glistening, monoclinic prisms melting at 171° , the corresponding *di- α -naphthoxy-* compound melts at 195° and the isomeric *di- β -naphthoxy-* derivative at 179° .

Di-methylacryldi- α -naphthylethylenediamine,



forms a microscopic, crystalline powder melting at 244 — 247° and sparingly soluble in most solvents with the exception of chloroform. The corresponding normal condensation products were not obtained in a pure state.

Di-phenoxyisobutyryldi- β -naphthylethylenediamine,



melts at 192° and the corresponding *di- β -naphthoxy-* derivative at 179° .

Small amounts of other crystalline products have been obtained in several of the reactions, but have not been investigated.

J. J. S.

Bromination of 1:5-Diaminoanthraquinone. ROLAND SCHOLL and H. BERBLINGER (*Ber.*, 1904, 37, 4180—4184).—The bromination of 1:5-diaminoanthraquinone proceeds differently according to the presence or absence of water. When the reaction is carried out in glacial acetic acid solution, or when the dry compound is exposed to bromine vapour, products containing a high proportion of bromine are obtained. These are, however, unstable, the excess of bromine being removed by exposure under reduced pressure, or by means of sodium hydrogen sulphite, the product in each case being the dibromo-derivative. The intermediate product appears to be a perbromide (compare Fries, *Abstr.*, 1904, i, 571). On the addition of water to the perbromide, the loosely combined bromine enters the nucleus, forming tetrabromodiaminoanthraquinone. The same compound is obtained when the bromination is carried out from the first in the presence of water.

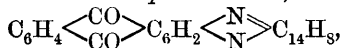
2:6-Dibromo-1:5-diaminoanthraquinone crystallises from nitrobenzene in steel-blue needles and melts at 274°. It dissolves readily in warm concentrated sulphuric acid, the crystalline *sulphate* being precipitated on cooling or slightly diluting the solution. The *tetra-acetyl* derivative forms yellow, prismatic needles which char at about 240°, and dissolves in concentrated nitric acid at 0°, being precipitated unchanged by water. The proof of the orientation given above will form the subject of a later communication.

2:4:6:8-Tetrabromo-1:5-diaminoanthraquinone, prepared as above, crystallises from nitrobenzene in needles resembling the dibromo-compound and melts above 300°. The *tetra-acetyl* derivative forms yellow needles and chars above 220°.

C. H. D.

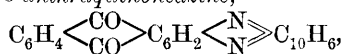
2:3-Diaminoanthraquinone and Azines of the Anthraquinone Series. ROLAND SCHOLL and PHILIPP KAČER (*Ber.*, 1904, 37, 4531—4534. Compare this vol., i, 70, 102).—2:3-Diaminoanthraquinone, obtained by the reduction of the 3-nitro-2-amino-derivative (*loc. cit.*) with aqueous sodium sulphide, separates from nitrobenzene in brownish-red crystals which do not melt at 320°. The *sulphate*, $C_6H_4 \cdot (CO)_2 \cdot C_6H_2(NH_2, H_2SO_4)_2$, forms a grey, crystalline powder, which is hydrolysed in contact with much water. The *diacetyl* derivative is yellow and crystallises from nitrobenzene.

9':10'-Phenanthra-2:3-anthraquinoneazine,



obtained by condensing 2:3-diaminoanthraquinone with phenanthraquinone in acetic acid solution, crystallises from nitrobenzene in compact, yellow needles which do not melt at 320°. It becomes strongly electrified when powdered, dissolves in concentrated sulphuric acid to a carmine-red solution, and does not yield a blue *N*-dihydroazine dye (*Abstr.*, 1904, i, 110) on treatment with alkaline hyposulphite solution.

1' : 2'-Naphtha-2 : 3-anthraquinoneazine,



obtained by condensing the diamino-compound with β -naphthaquinone, crystallises from cumene in yellow needles which melt above 320° .

Benzil condenses with the diamino-compound yielding $\alpha\beta$ -diphenyl-2 : 3-anthraquinoxalinequinone, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \diagup \text{N} \cdot \text{CPh} \diagdown \\ \diagdown \text{N} \cdot \text{CPh} \diagup \end{array}$, which crystallises from acetic acid in yellowish-brown needles melting at 271° .
J. J. S.

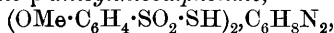
Action of Phenylhydrazine on Arylthiosulphonated Ethyl Acetoacetates. JULIUS TRÖGER and FRANZ VOLKMER (*J. pr. Chem.*, 1904, [ii], 70, 375—392. Compare Abstr., 1900, i, 494).—Ethyl arylthiosulphonacetoacetates, $\text{SO}_2\text{R} \cdot \text{S} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, react with phenylhydrazine in warm alcohol or glacial acetic acid solution to form 1-phenyl-3-methylpyrazolone-4-ketophenylhydrazone (Buchka and Sprague, Abstr., 1890, 28), but with phenylhydrazine in ethereal solution they form phenylhydrazones of arylthiosulphonacetoacetylphenylhydrazides, $\text{NHPh} \cdot \text{N} : \text{CMe} \cdot \text{CH}(\text{S} \cdot \text{SO}_2\text{R}) \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$. These remain unchanged when boiled with alcohol.

The following new ethyl arylthiosulphonacetoacetates are described : $\text{R} = o\text{-C}_7\text{H}_7$ is a viscid, yellow oil ; $\text{R} = 3 : 4\text{-C}_6\text{H}_3\text{Me}_2$ is a viscid, brown oil ; $\text{R} = p\text{-C}_6\text{H}_4\text{Cl}$ crystallises in rhombic plates and melts at $56\text{—}57^\circ$; $\text{R} = p\text{-C}_6\text{H}_4\text{Br}$ crystallises in plates and melts at $70\text{—}71^\circ$; $\text{R} = p\text{-C}_6\text{H}_4\text{I}$ crystallises in colourless needles and melts at $90\text{—}91^\circ$; $\text{R} = p\text{-C}_6\text{H}_4(\text{OMe})$ is a viscid, yellow oil.

The following phenylhydrazones of arylthiosulphonacetoacetylphenylhydrazides have been prepared : $\text{R} = p\text{-C}_7\text{H}_7$ crystallises in white, slender needles or leaflets and melts at $163\text{—}164^\circ$; $\text{R} = o\text{-C}_7\text{H}_7$ crystallises in matted, white needles and melts and decomposes at $145\text{—}146^\circ$; $\text{R} = \text{C}_6\text{H}_5$ crystallises in white needles and melts at $134\text{—}135^\circ$; $\text{R} = \beta\text{-C}_{10}\text{H}_7$ forms slender needles or yellow leaflets and melts and decomposes at $156\text{—}157^\circ$; $\text{R} = \alpha\text{-C}_{10}\text{H}_7$ crystallises in long, thin needles and melts and decomposes at $139\text{—}140^\circ$; $\text{R} = 3 : 4\text{-C}_6\text{H}_3\text{Me}_2$ is a yellow powder and melts and decomposes at 150° ; $\text{R} = p\text{-C}_6\text{H}_4\text{Cl}$ is a white, crystalline powder and melts and decomposes at $160\text{—}161^\circ$; $\text{R} = p\text{-C}_6\text{H}_4\text{Br}$ forms a white, crystalline mass and melts and decomposes at $168\text{—}169^\circ$; $\text{R} = p\text{-C}_6\text{H}_4\text{I}$ crystallises in slender, white needles and melts and decomposes at $167\text{—}168^\circ$; $\text{R} = p\text{-C}_6\text{H}_4(\text{OMe})$ forms a white, crystalline mass and melts and decomposes at $135\text{—}136^\circ$.

Sodium arylthiosulphonates, required for the preparation of ethyl arylthiosulphonacetoacetates, are best prepared by heating the concentrated aqueous solution of the corresponding sodium arylsulphinates with freshly precipitated sulphur. They are characterised by formation of the crystalline *p*-phenylenediamine salts.

p-Phenylenediamine *p*-anisylthiosulphonate,



melts at 161° to a blue liquid. *p*-Phenylenediamine 1 : 3 : 4-xylylthio-

sulphonate crystallises in thin leaflets and melts to a blue liquid at 157°. *p*-Phenylenediamine *p*-iodophenylthiosulphonate crystallises in small leaflets and melts at 155—156°. G. Y.

Separation of Aldoses by Secondary Hydrazines. RUDOLF OFNER (*Ber.*, 1904, 37, 4399—4402. Compare Abstr., 1904, i, 936).—The separation of phenylmethylglucosazone, prepared from dextrose and phenylmethylhydrazine, is assisted by the addition of a nucleus of the same substance prepared from *d*-fructose.

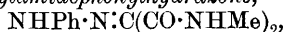
The presence of acetic acid does not prevent the separation of hydrazones. Dextrosephenylmethylhydrazone, xylosephenylmethylhydrazone, and xylosephenylbenzylhydrazone were respectively separated from solutions which contained free acetic acid. A. McK.

The Phenylmethylhydrazine Reaction of Fructose. CARL NEUBERG (*Ber.*, 1904, 37, 4616—4618).—Dextrose does not yield an osazone by the action of phenylmethylhydrazine according to Ofner's method (Abstr., 1904, i, 936; preceding abstract), whilst *d*-fructose does.

The formation of an osazone, observed by Ofner by the prolonged action of phenylmethylhydrazine on dextrose, is caused possibly by the transformation of dextrose into *d*-fructose as stated by de Bruyn and van Ekenstein. A. McK.

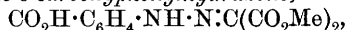
Dimethyl Mesoxalate-phenylhydrazone and its Derivatives. CARL BÜLOW and AUGUST GANGHOFFER (*Ber.*, 1904, 37, 4169—4179. Compare Bülow, Abstr., 1900, i, 56; 1901, i, 98; 1902, i, 325, 649; Eibner, Abstr., 1903, i, 871).—The authors' investigations lead to the conclusion that when an aromatic diazonium compound combines with a fatty compound containing an acid methylene group, the product is an azo-compound in all cases where the ketonic group can change into the enolic group. In all other cases a hydrazone is obtained.

Methyl mesoxalatephenylhydrazone, $\text{NHPh}\cdot\text{N}:\text{C}(\text{CO}_2\text{Me})_2$, prepared from diazobenzene chloride and methyl malonate, melts at 62° (compare R. Meyer, Abstr., 1891, 922). Ammonia converts it into *mesoxamidephenylhydrazone*, $\text{NHPh}\cdot\text{N}:\text{C}(\text{CO}\cdot\text{NH}_2)_2$, crystallising from acetic acid in yellow needles melting at 231—232°. Methylamine forms *mesoxalobismethylamidophenylhydrazone*,



crystallising from alcohol in yellow needles and melting at 117—118°. It dissolves in alkali hydroxides, thus reacting in the tautomeric form, $\text{CHPh}\cdot\text{N}:\text{C}[\text{C}(\text{OH})\cdot\text{NMe}]_2$.

Methyl mesoxalate-o-carboxyphenylhydrazone,



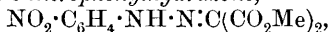
from methyl malonate and diazotised *o*-aminobenzoic acid, crystallises from alcohol in small, yellow needles melting at 186—187°. The *diamide* forms yellow needles melting at 275°; the *bismethylamide* melts at 247°.

Methyl mesoxalate-m-carboxyphenylhydrazone, from methyl malonate and diazotised *m*-aminobenzoic acid, crystallises from dilute alcohol in

yellow needles melting at 157—158°. The *diamide* melts above 285° and the *bismethylamide* at 247—248°.

Methyl mesoxalate-p-carboxyphenylhydrazone forms yellow needles melting and decomposing at 238°. Boiling sodium hydroxide hydrolyses it to *mesoxalic acid p-carboxyphenylhydrazone*, melting and decomposing at 275°. *Mesoxamidephenylhydrazone-p-carboxylic acid* forms yellow crystals melting above 285°. The *bismethylamide* melts above 285°.

Methyl mesoxalate-o-nitrophenylhydrazone,



from methyl malonate and diazotised *o*-nitroaniline, forms slender needles and melts at 143—144°; the *bismethylamide* melts at 186—187°.

Methyl mesoxalate-m-nitrophenylhydrazone melts at 115—116°; the *diamide* forms brownish-yellow crystals and melts at 235°; the *bismethylamide* forms yellow, felted needles and melts at 202—203°.

Methyl mesoxalate-p-nitrophenylhydrazone forms yellow needles melting at 162—163°; the *diamide* melts above 285°; the *bismethylamide* forms yellow, felted needles and melts at 243°.

Methyl mesoxalate-o-tolylhydrazone forms dark yellow needles melting at 75—76°; the *m-tolylhydrazone* forms yellow crystals melting at 63°; the *p-tolylhydrazone* melts at 89—90°, its *diamide* at 173—174°, and its *bismethylamide* at 91°.

Methyl mesoxalate-o-anisylhydrazone forms thick, yellow needles melting at 112—113°, and its *diamide* melts at 143°; the *p-anisylhydrazone* melts at 91°.

Methyl mesoxalate-as-m-xylylhydrazone forms slender, yellow needles melting at 93°.

Bülow's reaction (violet coloration with concentrated sulphuric acid and potassium dichromate) is given by those hydrazones which do not contain a para-substituent, except the nitro- and methoxy-derivatives.

C. H. D.

[Action of Amyl Nitrite on Phenyl-*m*-nitrobenzylidenehydrazine]. GAETANO MINUNNI (*Gazzetta*, 1904, 34, ii, 276—280).—According to the author, the compound I of Bamberger and Pemsel (*Abstr.*, 1903, i, 285) is diphenyldi-*m*-nitrobenzylidenehydrotetrazone (Minunni, *Abstr.*, 1898, i, 190), their compound III (given as (2) in the abstract quoted above) being dehydrophenyl-*m*-nitrobenzylidenehydrazone (*Abstr.*, 1898, i, 190) and compound V (given as (4) in the abstract) isodehydrophenyl-*m*-nitrobenzylidenehydrazone (*loc. cit.*). T. H. P.

3:6-Dimethylpyridazine. CARL PAAL and CARL KOCH (*Ber.*, 1904, 37, 4382—4387. Compare *Abstr.*, 1903, i, 290).—3:6-Dimethylpyridazine, $\text{CMe} \begin{smallmatrix} \text{N} & \text{N} \\ \diagdown & \diagup \\ \text{CH} & \text{CH} \end{smallmatrix} \text{CMe}$, prepared either by heating dimethylpyridazinedicarboxylic acid with 5 per cent. hydrochloric acid in sealed tubes at 200°, or by heating the potassium salt of dimethylpyridazinedicarboxylic acid, distils without decomposition at 214—215°, or at 109—110° under 20 mm. pressure, and solidifies to a

colourless, hygroscopic, crystalline mass melting in sealed capillary tubes at 32° . The *hydrochloride* crystallises in colourless, flat needles and plates melting at 184° ; the *aurichloride*, $C_6H_8N_2 \cdot HAuCl_4$, forms yellow needles melting at 170° ; the *platinichloride*, $(C_6H_8N_2)_2 \cdot H_2PtCl_6$, forms dark reddish-brown crystals decomposing above 200° ; the *mercurichloride* from the hydrochloride, $C_6H_8N_2 \cdot HCl \cdot 2HgCl_2$, separates in needles which melt at 140° , whereas the base forms a compound, $C_6H_8N_2 \cdot HgCl_2$, melting at 115° ; the *picrate* crystallises in yellow, silky, glistening needles melting at 164° .

3 : 6-Dimethylhexahydropyridazine, $CHMe \begin{smallmatrix} \text{NH} \cdots \text{NH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} CHMe$, prepared by the reduction of dimethylpyridazine with sodium and alcohol, is a colourless, clear liquid boiling at 180° ; the *hydrochloride* crystallises in colourless, concentrically-grouped prisms melting at 164° .

E. F. A.

Condensation of Aminoacetone with Benzaldehyde. THEODOR ALEXANDER (*Monatsh.*, 1904, 25, 1073—1080. Compare Pomeranz, *Abstr.*, 1894, i, 552).—When shaken in a dilute aqueous solution of sodium hydroxide, aminoacetone and benzaldehyde condense to form the *dihydropyrazine* compound, $CMe \begin{smallmatrix} \text{N} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{N} \end{smallmatrix} C \cdot \text{CH} : \text{CHPh}$; it is a viscid, yellow liquid which boils at 151° under 10 mm. pressure. The *hydrochloride*, $C_{13}H_{14}N_2 \cdot HCl$, is a white, hygroscopic substance; the *platinichloride*, $(C_{13}H_{14}N_2)_2 \cdot H_2PtCl_6$, is obtained as an orange-yellow, crystalline precipitate. On reduction with sodium in amyl-alcoholic solution, the condensation product yields the di-acid base, $C_{13}H_{20}N_2$, which is a colourless, mobile liquid, has an aromatic odour, and boils at 153° under 11 mm. pressure. The *hydrochloride*, $C_{13}H_{20}N_2 \cdot 2HCl$, is a white, crystalline, hygroscopic substance.

When heated with water and a few drops of hydrochloric acid in a sealed tube at 180° , the condensation product is decomposed with formation of benzaldehyde.

G. Y.

Interaction of Zinc Ethyl and Benzenediazonium Chloride. III. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1052—1055. Compare *Abstr.*, 1903, i, 441, and 1904, i, 268).—Besides the compounds already given as formed in this reaction (*loc. cit.*) there results also:

1-Ethyl-2 : 3 : 4-trihydrocinnoline, $C_{10}H_4N_2$, which boils at $90-96^{\circ}$ under 13 mm. pressure and is soluble in 7 per cent. hydrochloric acid, from which it is precipitated unchanged by the addition of sodium hydroxide.

The author considers that the benzenediazonium chloride is first converted into a hypothetical ethyldiazobenzene, which, under the influence of zinc ethyl, and later of water, combines with the elements of ethane to give phenyldiethylhydrazine, $NEtPh \cdot NH_2Et$. The latter then loses 2 atoms of hydrogen with the formation of a second six-carbon ring.

T. H. P.

Action of Zinc Ethyl on Phenylazoethane. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1056—1062. Compare preceding abstract).—The action of zinc ethyl on phenylazoethane in ethereal solution yields phenyldiethylhydrazine, $\text{NHPh}\cdot\text{NEt}_2$, *s*-ethylphenylhydrazine, and 1-ethyl-2 : 3 : 4-trihydrocinnoline.

T. H. P.

An Oxidation Product of Amino-orcinol Mono-methyl Ether. FERDINAND HENRICH and F. SCHIERENBERG (*J. pr. Chem.*, 1904, [ii], **70**, 365—374. Compare Abstr., 1897, i, 446; 1903, i, 414; 1904, i, 494).—When amino-orcinol mono-methyl ether (1 mol.) is dissolved in aqueous potassium hydroxide (2 mols.) and a current of air passed through the solution for a week, the phenoxazine derivative, $\text{C}(\text{OMe})\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{OMe})\cdot\text{C}(\text{OMe})\cdot\text{CH}(\text{CO}\cdot\text{CH}:\text{C}\cdot\text{O}\cdot\text{C}(\text{NH}_2)\cdot\text{OMe})$, is produced. It crystallises in matted, red needles, melts at 256—260°, is easily soluble in warm ethyl acetate, benzene, or glacial acetic acid, and dissolves in concentrated sulphuric acid to a violet solution. When treated with sodium nitrite in dilute hydrochloric acid solution, it forms an intensely blue solution, which, with evolution of gas, deposits a brown, flocculent precipitate. When boiled with alcoholic alkali hydroxides, the phenoxazine derivative is decomposed. The *hydrochloride*, $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2\cdot\text{HCl}$, crystallises in green leaflets and is hydrolysed by warm water; the *hydrobromide*, $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2\cdot\text{HBr}$, is green. When heated with aluminium chloride at 210—220°, or with concentrated hydrochloric acid at 200°, the phenoxazine derivative yields methyl chloride and, with the latter, a *product*, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$ (?), which resembles the archil dyes. The *acetyl derivative*, $\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}_2\text{Ac}$, crystallises in clusters of yellow needles, decomposes above 265°, and dissolves in concentrated hydrochloric acid to a dark orange-coloured solution, which, on addition of ether, deposits a *hydrochloride*.

Reduction of the phenoxazine derivative with stannous chloride and hydrochloric acid leads to the formation of the *dihydrochloride* of a dihydrophenoxazine compound, $\text{C}_{15}\text{H}_{16}\text{O}_3\text{N}_2\cdot 2\text{HCl}$, which crystallises in white, silky needles, yields the phenoxazine derivative when treated with aqueous alkali hydroxides, dissolves in concentrated sulphuric acid to a bluish-green solution, and gives an intensely blue coloration and a dark red substance when treated with sodium nitrite solution. The *triacetyl derivative*, $\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_2\text{Ac}_3$, obtained by the action of acetic anhydride and sodium acetate on the hydrochloride, crystallises in sheaves of red needles, melts at 166—167°, gives a yellow, changing to red, and finally to blue, coloration with concentrated sulphuric acid, and dissolves in concentrated hydrochloric acid to a dark green, in nitric acid to a red solution.

Simultaneous reduction and acetylation of the phenoxazine derivative by means of zinc dust, glacial acetic acid, and acetic anhydride leads to the formation of the *diacetyl derivative* of the dihydrophenoxazine compound, $\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2\text{Ac}_2$, which crystallises in colourless leaflets or sheaves of short needles, melts at 211—212°, is easily soluble in alcohol, chloroform, ethyl acetate, or glacial acetic acid, and

dissolves in concentrated sulphuric acid to a red, changing to a green, and in concentrated hydrochloric acid to a green, changing to a red, solution; with sodium nitrite, it gives an orange coloration.

The action of bromine on the phenoxazine derivative in glacial acetic acid solution leads to the formation of the *bromo-compound*, $C_{15}H_{13}O_3N_2Br$, which melts at 212° . G. Y.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XV. The Metallic Derivatives of the Condensation Products of Acyl-hydrazines with Aldehydes and Ketones, and their Behaviour towards Acid Chlorides and Iodine. ROBERT STOLLÉ and ED. MÜNCH (*J. pr. Chem.*, 1904, [ii], 70, 393—422. Compare Abstr., 1903, i, 721; 1904, i, 102, 200, 453, 626, 627, 694, 695, 696, 697).—*Sodium benzoylbenzylidenehydrazine*, $CHPh:N\cdot NNaBz$, is precipitated as a white powder on addition of ether to the solution of benzoylhydrazine in alcoholic sodium hydroxide; the *silver* derivative, $CHPh:N\cdot NAg\cdot Bz$, formed on addition of silver nitrate to the solution of benzoylhydrazine and sodium ethoxide (1 mol.) in alcohol, is a white powder, which becomes brown on exposure to light and commences to decompose at 100° ; the *mercurichloride* derivative is a white, crystalline powder.

Benzoyl-p-tolylidenehydrazine, $C_7H_7\cdot CH:N\cdot NHBz$, crystallises in colourless, strongly refractive needles and melts at 155° ; the *silver* derivative, $C_{15}H_{13}ON_2Ag$, is a white powder which decomposes at 180° .

Benzoylfurfurylidenehydrazine melts at 182° (m. p. 179° ; Minunni and Carta-Satta, Abstr., 1900, i, 251); the *silver* derivative is a yellow powder.

The *silver* derivative of acetylbenzylidenehydrazine, $C_9H_9ON_2Ag$, decomposes with evolution of a gas at 227° ; the *mercurichloride* derivative, $C_9H_9ON_2\cdot HgCl$, is a white, crystalline powder.

Benzylethylidenehydrazine, $CHMe:N\cdot NHBz$, crystallises in glistening leaflets and melts at 162° ; when dissolved in an alcoholic solution of 1 mol. of sodium ethoxide and treated with silver nitrate, it yields a white precipitate which rapidly decomposes.

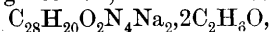
The action of chloral hydrate on benzoylhydrazine in ethereal solution at 35° leads to the formation of an *additive* compound, $NHBz\cdot NH\cdot CH(OH)\cdot CCl_3$, which is obtained on evaporation of the solution in colourless crystals; it melts at 72° with formation of the *condensation* product, $NHBz\cdot N\cdot CH\cdot CCl_3$, which is also formed by heating benzoylhydrazine with chloral hydrate on the water-bath. This crystallises in slender needles and melts and decomposes at 194° .

When heated together at 120° , benzoylhydrazine and benzophenone form the *additive* compound, $NHBz\cdot NH\cdot CPh_2\cdot OH$, which crystallises in colourless, refractive, slender needles, and melts and is converted into the *condensation* product at 108° .

The *silver* derivative of the *condensation* product, $C_{20}H_{15}ON_2Ag$, is a yellow powder which is fairly stable towards light; the *mercuric* derivative, $(C_{20}H_{15}ON_2)_2Hg$, crystallises in colourless needles and melts at 241° .

The *sodium* derivative, $C_{16}H_{12}O_2N_4Na_2 \cdot 2C_2H_6O$, the *silver* derivative, $C_{16}H_{12}O_2N_4Ag_2$, and the *mercuric* derivative, $C_{16}H_{12}O_2N_4Hg \cdot 2C_2H_6O$, of dibenzoyl glyoxalosazone are described.

The *monosodium* derivative of dibenzoylbenzilozazone, $C_{23}H_{21}O_2N_4Na$, crystallises in glistening needles; the *disodium* derivative,



loses $2C_2H_6O$ at 120° ; the *monosilver* derivative, the *disilver* derivative, and the *dimercurichloride* derivative, $C_{28}H_{20}O_2N_4(HgCl)_2$, are described.

4-Benzoyl-2:5-diphenyl-4:5-dihydro-1:3:4-oxadiazole (Abstr., 1904, i, 102) forms thick, colourless crystals and melts at 138° . When boiled with dilute sulphuric acid, it is hydrolysed to dibenzoylhydrazine and benzaldehyde.

4-Acetyl-2:5-diphenyl-4:5-dihydro-1:3:4-oxadiazole crystallises in colourless needles, melts at 98° , and is hydrolysed by dilute acids to benzoylacetylhydrazine and benzaldehyde, which react in warm dilute acids to form benzoylbenzylidenehydrazine and acetic acid.

4-Benzoyl-5-phenyl-2-methyl-4:5-dihydro-1:3:4-oxadiazole crystallises in large, colourless crystals and melts at 53° . It reduces ammoniacal silver nitrate on prolonged boiling, especially in presence of sodium hydroxide; when boiled with dilute acids, it yields benzoylbenzylidenehydrazine.

4-Acetyl-5-phenyl-2-methyl-4:5-dihydro-1:3:4-oxadiazole crystallises in slender, white needles, melts at 91° , reduces ammoniacal silver nitrate slowly at the ordinary temperature, and is hydrolysed by very dilute alcoholic hydrochloric acid at the ordinary temperature to diacetylhydrazine and acetylbenzylidenehydrazine, by boiling alcoholic hydrochloric acid to benzaldehyde, hydrazine, and acetic acid.

4-Benzoyl-2:5:5-triphenyl-4:5-dihydro-1:3:4-oxadiazole crystallises in slender, colourless needles and melts at 131° .

Diphenyloxadiazole is formed by the action of iodine on the silver or the mercurichloride derivatives of benzoylbenzylidenehydrazine, or by oxidation of benzoylbenzylidenehydrazine with potassium ferricyanide or amyl nitrite. *p-Tolylphenyl-1:3:4-oxadiazole*, obtained by the action of iodine on benzoyl-*p*-tolylidenehydrazine suspended in ether, crystallises in leaflets and melts at 126° ; the *additive* compound, $C_{15}H_{12}ON_2 \cdot AgNO_3$, crystallises in white, glistening needles and melts and decomposes at 258° .

Phenylfuryl-1:3:4-oxadiazole, formed by the action of iodine on the silver derivative of benzoylfurfurylidenehydrazine, crystallises in colourless leaflets, melts at 105° , and forms the *additive* compound, $C_{12}H_8O_2N_2 \cdot AgNO_3$, which crystallises in soft, white needles and decomposes at 215° .

The action of iodine on the mercuric derivative of benzophenone-benzoylhydrazine in ethereal solution leads to the formation of diphenylketazine and 4-benzoyl-2:5:5-triphenyl-4:5-dihydro-1:3:4-oxadiazole.

Diphenylbisoxadiazole, $\begin{array}{c} N-N \\ | \quad | \\ CPh \cdot O \end{array} > C \cdot C < \begin{array}{c} N \cdot N \\ | \quad | \\ O-CPh \end{array}$, is formed by the

action of iodine on the mercuric derivative of glyoxaldibenzoylosazone in ethereal solution, or by heating dibenzoyloxallylhydrazine with phosphoric oxide. It crystallises in slender, white, glistening needles,

melts at 270°, and is hydrolysed by dilute hydrochloric acid at 150° to benzoic acid and hydrazine hydrochloride. G. Y.

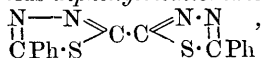
Formation of Heterocyclic Compounds from Hydrazine Derivatives. XVI. Diazoles and Bisdiazoles. ROBERT STOLLÉ and W. KIND (*J. pr. Chem.*, 1904, [ii], **70**, 423—432).—When heated with phosphoric oxide, benzoylhydrazine yields 2:5-diphenyl-1:3:4-oxadiazole, 2:5-diphenyl-1:3:4-triazole, and 3:6-diphenyl-1:4-dihydro-1:2:4:5-tetrazine. When heated with phosphorus pentasulphide in a vacuum at 210°, benzoylhydrazine forms diphenylthiodiazole, $\begin{array}{c} \text{N} \cdots \text{CPh} \\ | \quad \quad | \\ \text{N} \cdots \text{CPh} \end{array} > \text{S}$, which crystallises in glistening scales and melts at 141—142°. It is formed also when benzylidenebenzoylhydrazine or benzylideneazine is heated with phosphorus pentasulphide.

Diacetyloxalyldiazine, $\text{NHAc} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHAc} \cdot \text{H}_2\text{O}$, formed when oxalyldiazine is heated for one hour at 140° with acetic anhydride, crystallises in glistening, white scales, melts at 276°, is easily soluble in hot water or dilute alkali hydroxides or ammonia, reduces ammoniacal silver nitrate and Fehling's solutions only on prolonged warming, and on prolonged boiling with dilute acids is hydrolysed to acetic and oxalic acids and hydrazine. *Hexa-acetyloxalyldiazine*, formed when oxalyldiazine is boiled with acetic anhydride in a reflux apparatus for two days, crystallises in delicate needles, melts at 156—158°, and is hydrolysed to oxalyldiazine when boiled with water.

Dimethylbisoxadiazole, $\begin{array}{c} \text{N} \cdots \text{N} \\ | \quad \quad | \\ \text{CMe} \cdot \text{O} \end{array} > \text{C} \cdot \text{C} < \begin{array}{c} \text{N} \cdots \text{N} \\ | \quad \quad | \\ \text{O} \cdot \text{CMe} \end{array}$, is formed when diacetyloxalyldiazine is heated with phosphoric oxide in a vacuum or when hexa-acetyloxalyldiazine is heated in a vacuum at 180—240°, or when oxalyldiazine is boiled for two days with acetic anhydride and the product distilled under reduced pressure. It crystallises in slender, colourless needles, melts at 212°, and sublimes without decomposing; the *silver nitrate additive* compound, $\text{C}_6\text{H}_6\text{O}_2\text{N}_4 \cdot 2\text{AgNO}_3$, crystallises in needles and melts and decomposes at 215°.

Dimethylbisthiodiazole, $\begin{array}{c} \text{N} \cdots \text{N} \\ | \quad \quad | \\ \text{CMe} \cdot \text{S} \end{array} > \text{C} \cdot \text{C} < \begin{array}{c} \text{N} \cdots \text{N} \\ | \quad \quad | \\ \text{S} \cdot \text{CMe} \end{array}$, obtained by heating diacetyloxalyldiazine with phosphorus pentasulphide at 125—150°, crystallises in colourless, matted needles, melts at about 238°, sublimes without decomposition, and forms an *additive* compound with silver nitrate, $\text{C}_6\text{H}_6\text{N}_4\text{S}_2 \cdot 2\text{AgNO}_3$, which crystallises in silky needles.

Dibenzoyloxalyldiazine, formed by the action of benzoic chloride and sodium hydroxide on oxalyldiazine, crystallises in white needles and melts at 278°. When heated with phosphorus pentasulphide in a vacuum at 200°, it yields *diphenylbisthiodiazole*,



which forms a loose, white powder, commences to sinter at 245°, and is completely melted at 252°. G. Y.

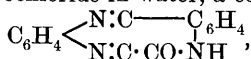
Formation of Heterocyclic Compounds from Hydrazine Derivatives. XVII. Diphenylosotetrazine and Diphenylosotriazole. ROBERT STOLLÉ, ED. MÜNCH, and W. KIND (*J. pr. Chem.*, 1904, [ii], 70, 433—441).—2 : 3-Dibenzoyl-5 : 6-diphenyl-2 : 3-dihydro-

1 : 2 : 3 : 4-tetrazine, $\begin{array}{c} \text{CPh:N}\cdot\text{NBz} \\ | \\ \text{CPh:N}\cdot\text{NBz} \end{array}$, is formed by the action of iodine on the silver derivative of dibenzoylbenzilozazone in carbon tetrachloride solution, and on the mercurichloride derivative of dibenzoylbenzilozazone suspended in ether, and by the oxidation of benzil-dibenzoylosazone with potassium ferrieyanide and alkaline solution. It crystallises with 1 mol. of alcohol of crystallisation, which is lost at 100°; when dried at 100° is a white, voluminous powder, and melts at 189°. When boiled with dilute hydrochloric acid in alcoholic solution, it yields 2-benzoyl-5 : 6-diphenyl-2 : 3-dihydro-1 : 2 : 3 : 4-tetrazine, which crystallises in slender, colourless needles, melts at 248°, and is soluble in dilute sodium hydroxide or ammonia. The silver derivative, $\text{C}_{21}\text{H}_{15}\text{ON}_4\text{Ag}$, is an amorphous, yellow powder; the mercurichloride derivative, $\text{C}_{21}\text{H}_{15}\text{ON}_4\cdot\text{HgCl}$, is a white powder.

When boiled with concentrated hydrochloric acid and alcohol, the dibenzoyl compound is hydrolysed to 5 : 6-diphenyl-2 : 3-dihydro-1 : 2 : 3 : 4-tetrazine, which crystallises in thick needles and melts at 135° (Abstr., 1904, i, 201). It is oxidised to a yellow oil by lead peroxide and sulphuric acid; when heated with hydrochloric acid at 125°, it forms the hydrochloride; at higher temperatures, it is decomposed to a viscid, yellow oil, which contains hydrazine. The hydrochloride, $\text{C}_{14}\text{H}_{12}\text{N}_4\cdot\text{HCl}$, melts at 183—185°. The benzyldiene derivative, $\text{C}_{21}\text{H}_{16}\text{N}_4$, crystallises in matted needles and melts at 184°. When treated with bromine in hot alcoholic solution, diphenyldihydrotetrazine yields α -tolane dibromide, which melts at 205—206°. The action of nitrous acid on diphenyldihydrotetrazine in ethereal solution leads to the formation of 3 : 4-diphenyl-1 : 2 : 5-triazole, which crystallises in slender, white needles and melts at 138°; the silver derivative, $\text{C}_{14}\text{H}_{10}\text{N}_3\text{Ag}$, is sensitive to light. G. Y.

A Colourless Hydrochloride of Rosaniline. RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, 37, 4326—4327. Compare Abstr., 1904, i, 877; ii, 794).—When rosaniline is crystallised from 2 parts of 30 per cent. hydrochloric acid and the crystals washed with the free acid, a colourless, crystalline hydrochloride is obtained. The analyses agree fairly well with the formula $\text{C}_{20}\text{H}_{11}\text{ON}_3\cdot 2\text{HCl}\cdot 4\text{H}_2\text{O}$. It dissolves in cold water yielding a nearly colourless solution, but when heated yields the ordinary magenta solution. New magenta does not yield crystals under similar conditions. J. J. S.

Phthalonimide and o-Phenylenediamine. SIEGMUND GABRIEL (*Ber.*, 1904, 37, 4316).—On boiling a solution of phthalonimide and o-phenylenediamine hydrochloride in water, a compound,



is obtained, crystallising in yellow needles melting at 267—268°, and

evidently identical with the compound obtained by Manuelli and Silvestri (Abstr., 1904, i, 784) by condensing phthalonic acid with *o*-phenylenediamine and acting on the product with ammonia.

C. H. D.

Desmotropic Compounds. OTTO DIMROTH (*Annalen*, 1904, 335, 1—112. Compare Abstr., 1903, i, 127).—It is at present believed that there is a relation between the dissociating power of a solvent and its capacity to isomerise desmotropic compounds. In the cases previously studied (Menschutkin, Abstr., 1890, 1366; Stobbe, Abstr., 1903, i, 421), the coefficient of isomerisation increases with the dissociating power of the solvent; the reverse is found to be the case for the isomerisation of methyl 5-hydroxyphenyl-1:2:3-triazole-4-carboxylate into its keto-desmotrope. The following values for k have been found for the enolic ester: in methyl alcohol solution, at 25°, $k=0.00529$; in ethyl alcohol solution, at 0°, $k=0.000195$, at 18°, 0.00359, at 25°, 0.01017, $k_{25}/k_{15}=4.5$; in acetone, at 25°, $k=0.0527$; in ether, at 18°, $k=0.041$; in chloroform, at 0°, $k=0.00338$, at 18°, 0.0836, at 25°, 0.27, $k_{25}/k_{15}=5.27$; in a saturated aqueous solution, at 25°, $k=0.00023$, at 50°, 0.00126, $k_{50}/k_{40}=4.6$; in aqueous solution, 1.42 grams of enolic ester per 1500 c.c. water, at 50°, $k=0.000663$; 0.71 gram of enolic ester per 1500 c.c. water, at 50°, $k=0.000292$; in saturated aqueous solutions, at 50°, containing 2 mols. of the sodium derivative per mol. of enolic ester, $k=0.00225$, containing 1 mol. of hydrogen chloride per mol. of enolic ester, $k=0.00195$, containing 1.8 mols. of acetic acid per mol. of enolic ester, $k=0.00124$; and saturated in 0.06*N* sodium chloride solution, at 50°, $k=0.00106$.

As the conversion of methyl 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate into its keto-modification takes place most rapidly in anhydrous solvents, an additive compound with water cannot form an intermediate stage; neither can the isomerisation be the result of electrolytic dissociation, as k is found to diminish with dilution and to increase on addition of the sodium derivative of the enolic ester (compare Lapworth, *Trans.*, 1902, 81, 1508). The enolic ester can be estimated in presence of the keto-ester by addition of potassium iodide and iodate and titration of the liberated iodine with sodium thiosulphate, as the keto-ester does not take part in the reaction.

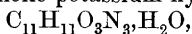
The anhydrous enolic ester melts at 74°, resolidifies and again melts at 82°, and gradually changes, at the ordinary temperature, into the keto-ester. It has the molecular conductivity μ_{∞} 371 at 25°; 484.5 at 50°. The dissociation constant diminishes with dilution: $V=94.3$, $100K=1.46$; $V=754.4$, $100K=1.09$. The sodium derivative of the enolic ester has the molecular conductivity μ_{∞} 75.3 at 25°, 113.5 at 50°.

When dissolved in ether, benzene, or chloroform, the enolic ester undergoes complete isomerisation; in methyl alcohol, a state of equilibrium is reached when the esters are in the proportion 1 of enolic ester:150 of keto-ester, in ethyl alcohol when the proportion is 1 of enolic ester:300 keto-ester, and in water 1 of enolic ester:14 of keto-ester.

The sodium derivative of the enolic ester crystallises in clusters of

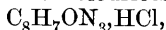
needles and loses water of crystallisation at 105° ; the *copper* derivative, $C_{20}H_{16}O_6N_6Cu, 2H_2O$, forms small, green crystals; the *silver* derivative is obtained as a white precipitate; the *ammonia* derivative is formed immediately by the action of ammonia on the enolic ester in alcoholic or ethereal solution, only slowly by the action of ammonia on the keto-ester in ethereal solution, or incompletely in benzene solution. The *aniline* compound, $C_{10}H_9O_3N_3, C_6H_7N$, formed by the action of aniline on the enolic ester, crystallises in slender needles and melts at 99° ; the *phenylhydrazine* compound, $C_{10}H_9O_3N_3, C_6H_5N_2$, is formed by the action of phenylhydrazine on the enolic ester in alcoholic solution, or on fusing the keto-ester with phenylhydrazine at 100° . It crystallises in white needles, melts at $140-141^{\circ}$, and, if heated to 145° and quickly cooled, yields the keto-ester and phenylhydrazine, but if allowed to cool slowly is regained unchanged. A solution of the phenylhydrazine compound, the keto-ester and phenylhydrazine in equilibrium is obtained on boiling the phenylhydrazine compound or the keto-ester and phenylhydrazine in alcohol. The *benzidine* compound, $C_{32}H_{30}O_6N_8$, is formed from benzidine and the enolic ester in alcoholic solution, and melts and decomposes into benzidine and keto-ester at 149° ; it is decomposed by dilute sodium carbonate solution or concentrated hydrochloric acid, but not by dilute hydrochloric acid; when boiled with methyl alcohol, it is almost completely decomposed into keto-ester and benzidine. The *dianisidine* compound, $C_{34}H_{34}O_8N_8$, crystallises in small prisms, melts and decomposes at 150° , and is partly decomposed when boiled with methyl alcohol. The *o-tolidine* compound, $C_{34}H_{34}O_6N_8$, formed by the action of *o*-tolidine on the enolic ester, crystallises as a white powder, melts at $145-146^{\circ}$, and is decomposed by aqueous sodium carbonate, but not by dilute hydrochloric acid; when fused or when boiled with alcohol, it yields an isomeric *substance* which is also formed by the action of *o*-tolidine on the keto-ester in alcohol; it crystallises in glistening, yellow needles, melts at 119° , and is decomposed by dilute hydrochloric acid, but not by sodium carbonate solution.

[With E. EBERHARDT.]—The *benzoyl* derivative of the enolic ester, $OBz \cdot C_2N_3Ph \cdot CO_2Me$, formed by the action of benzoic chloride on the sodium compound in ethereal solution, melts at $104-105^{\circ}$. The *ethyl ether*, $OEt \cdot C_2N_3Ph \cdot CO_2Me$, obtained by treating the silver compound with ethyl iodide, crystallises in plates, melts at $93-94^{\circ}$, and is hydrolysed by boiling alcoholic potassium hydroxide to the *acid*,



which, when anhydrous, melts and decomposes at $96-97^{\circ}$. 5-Ethoxy-1-phenyl-1:2:3-triazole, formed by heating the carboxylic acid at $100-105^{\circ}$, separates from light petroleum in small crystals and melts at $58-59^{\circ}$.

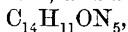
[With E. LETSCHE.]—5-Hydroxy-1-phenyl-1:2:3-triazole is best purified by conversion into the colourless *hydrochloride*,



which decomposes at $124-125^{\circ}$ and yields the hydroxytriazole when treated with water. The *sodium* compound, $C_8H_6ON_3Na$, crystallises in white needles; the *benzoyl* derivative, $C_2N_3HPh \cdot OBz$, formed by the action of benzoic chloride in pyridine solution, crystallises in slender, white needles and melts at $141-142^{\circ}$; with phenylhydrazine or

semicarbazide in alcoholic solution, it forms *s*-benzoylphenylhydrazine and benzoylsemicarbazide respectively, hydroxyphenyltriazole being re-formed.

[With E. EBERHARDT.]—5-Hydroxy-1-phenyltriazole “couples” with diazobenzene chloride in aqueous sodium carbonate solution, forming two substances: a scarlet compound, $C_{14}H_{11}ON_5$, which crystallises in needles and melts at $131-132^\circ$, and a colourless compound,



which crystallises in white leaflets and melts at $162-163^\circ$.

[With E. LETSCHE.]—When oxidised with potassium permanganate in aqueous sodium carbonate solution, 5-hydroxy-1-phenyl-1:2:3-triazole yields oxanilic acid, *p*-benzoquinone, and phenylisocyanide. When boiled with water, 1-phenyl-5-triazolone-4-carboxylic acid yields glycollic anilide and a substance, $C_{17}H_{14}O_4N_4$.

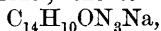
[With E. EBERHARDT.]—When treated with methyl alcohol, 1-phenyl-5-triazolone-4-carboxylic acid yields methoxyacetanilide and a substance, $C_{17}H_{14}O_4N_4$, which crystallises in colourless needles, melts at 168° , and with sodium methoxide in methyl alcoholic solution yields glycollic anilide and the sodium salt of hydroxyphenyltriazolecarboxylic acid. When warmed with fuming hydrochloric acid, hydroxyphenyltriazolonecarboxylic acid yields chloroacetanilide.

[With E. LETSCHE.]—5-Benzoxyl-1-phenyl-4-methyl-1:2:3-triazole melts at 91° and is easily hydrolysed by boiling dilute hydrochloric acid, by sodium ethoxide in cold alcoholic solution, and by phenylhydrazine and semicarbazide with formation of *s*-benzoylphenylhydrazine and benzoylsemicarbazide respectively. The action of methyl iodide on the sodium derivative of 5-hydroxy-1-phenyl-4-methyltriazole leads to the formation of a substance, $C_{20}H_{23}O_2N_6I$, which melts at 168° , has acid properties, gives a brownish-red coloration with ferric chloride, and yields the hydroxytriazole when warmed with aqueous sodium hydroxide or silver oxide; if an excess of methyl iodide is used for the methylation, a periodide which melts at 96° is formed.

The action of phenylhydrazine on 5-hydroxy-1-phenyl-4-methyltriazole leads to the formation of the phenylhydrazone of pyruvic anilide, $NHPh \cdot CO \cdot CMe : N \cdot NHPh$, which melts at 174° . When boiled with benzene, ether, chloroform, xylene, or toluene, the enolic compound yields a substance, $C_9H_8ON_2$, which melts at $163-164^\circ$ and is stable towards aqueous alkali hydroxides or acids.

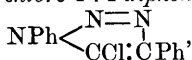
5-Hydroxy-1:4-diphenyl-1:2:3-triazole, $NPh < \begin{matrix} N \equiv N \\ C(OH) : CPh \end{matrix}$, is

obtained in the form of its sodium compound by the action of phenylazoisimide on ethyl phenylacetate in presence of sodium ethoxide. The hydroxytriazole, precipitated on addition of hydrochloric acid to the solution of the sodium compound, forms white crystals, melts at $150-151^\circ$, is moderately soluble in alcohol, insoluble in water, ether, or benzene, dissolves easily in aqueous alkali hydroxides, and gives no coloration with ferric chloride; the sodium compound,



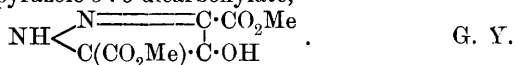
crystallises in stellate groups; the hydroxytriazole is completely oxidised by potassium permanganate at 40° . The benzoyl derivative crystallises in white needles and melts at 132° ; the methyl ether

crystallises in slender, white needles and melts at 126° . The action of phosphorus pentachloride on 5-hydroxy-1:4-diphenyltriazole leads to the formation of 5-chloro-1:4-diphenyltriazole,

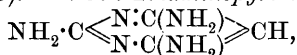


which crystallises in plates and melts at 137° .

[With E. EBERHARDT.]—The formation of methyl 1-phenyl-5-triazolone-4-carboxylate by the action of phenylazoimide on methyl malonate is accompanied by that of a small amount of a substance, $\text{C}_7\text{H}_8\text{O}_5\text{N}_2$, which melts at 232° , has acid properties, gives a violet coloration with ferric chloride, when heated at 250 — 260° evolves carbon dioxide and yields a crystalline product melting at 86 — 91° , and when heated with fuming hydrochloric acid in a sealed tube forms the hydrochloride of 4-hydroxypyrazole (Wolff, Abstr., 1900, i, 691). It must therefore be methyl 4-hydroxypyrazole-3:5-dicarboxylate,



2-Aminoadenine (2:6-Diaminopurine). WILHELM TRAUBE (*Ber.*, 1904, 37, 4544—4547. Compare Abstr., 1900, i, 416; 1901, i, 54, 762; 1904, i, 632, 633).—2:4:6-Triaminopyrimidine,

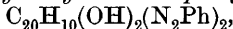


is readily obtained by the condensation of guanidine with malononitrile in alcoholic solution. Its *sulphate*, $\text{C}_4\text{H}_7\text{N}_5 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is sparingly soluble, and also the *nitrate*, whereas the *hydrochloride* dissolves readily in water. The base crystallises from dilute alcohol in colourless needles. Nitrous acid transforms it into an *isonitroso*-derivative, which, when reduced with ammonium sulphide, yields 2:4:5:6-tetraaminopyrimidine. This is best purified by means of its *sulphate*, $\text{C}_4\text{H}_8\text{N}_6 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. The free base crystallises from water in needles and reduces ammoniacal silver nitrate solution. A *formyl* derivative is obtained by boiling the above sulphate with formic acid and sodic formate; it crystallises in needles, melts at 152 — 155° , and at the same time loses water, yielding 2-aminoadenine (2:6-diaminopurine),

$\text{CH} \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{C}(\text{NH}_2) \cdot \text{N} \\ \diagdown \quad \diagup \\ \text{N} - \text{C} \cdot \text{N} = \text{C} \cdot \text{NH}_2 \end{array}$, which crystallises from water in

stout prisms. Its solution in nitric acid yields a crystalline precipitate with silver nitrate. It forms well-defined salts with mineral acids, the *nitrate* is very sparingly soluble, and the *platinichloride* crystallises in dark needles relatively readily soluble. J. J. S.

Azo-derivatives of 3:3'-Dihydroxy-2:2'-dinaphthyl and 3:3'-Dihydroxy-1:1'-dinaphthyl. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1904, [iii], 31, 1273—1277. Compare Abstr., 1904, i, 789).—3:3'-Dihydroxy-2:2'-dinaphthyl-1:1'-disazobenzene,



prepared by the interaction of 3:3'-dihydroxy-2:2'-dinaphthyl with diazobenzene (2 mols.), is an orange-coloured substance, insoluble in

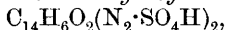
water, soluble in alcohol with a deep orange colour, and in sulphuric acid with a cherry-red colour. 3:3'-*Dihydroxy-1:1'-dinaphthyl-4-azo-benzene*, $C_{20}H_{18}O_2 \cdot N_2Ph$, obtained by the interaction of 3:3'-dihydroxy-1:1'-dinaphthyl with diazobenzene (1 mol.) is red, dissolves in alcohol with an orange colour, in sulphuric acid with a grey colour, and is insoluble in water. 3:3'-*Dihydroxy-1:1'-dinaphthyl-4:4'-disazobenzene* is dull red, gives a reddish-orange solution in alcohol, a wine-red liquid with sulphuric acid, and is insoluble in water. 3:3'-*Dihydroxy-1:1'-dinaphthyl-4-azo-m-toluene* is brownish-red, dissolves with this colour in alcohol and sulphuric acid, and is insoluble in water.

3:3'-*Dihydroxy-1:1'-dinaphthyl-4:4'-disazo-m-toluene* is red and gives solutions similar to those of the diazobenzene compound. The *disazo-p-nitrobenzene* derivative is bright red, gives a yellowish-orange coloration in alcohol, and greyish-green in sulphuric acid. The *product*, obtained by the interaction of 3:3'-dihydroxy-1:1'-dinaphthyl with benzidine, is violet, gives a purple solution in alcohol, and bluish-green with sulphuric acid. 3:3'-*Dihydroxy-1:1'-dinaphthyl-4:4'-disazo-β-naphthalene* is red, gives a bright red colour with a mixture of alcohol and xylene, and a blue coloration with sulphuric acid. The azo-dyes obtained from 3:3'-dihydroxy-1:1'-dinaphthyl are deeper, but less vivid, than those derived from *α-naphthol*, and, being insoluble, are capable of being printed directly. T. A. H.

Some Diazonium Salts of the Anthraquinone Series.

PHILIPP KAČER and ROLAND SCHOLL (*Ber.*, 1904, **37**, 4185—4187).—*Anthraquinone-1-diazonium hydrogen sulphate*, $C_{14}H_7O_2 \cdot N_2 \cdot SO_4H$, obtained by diazotising 1-aminoanthraquinone in sulphuric acid solution and precipitating the cooled solution with ether-alcohol, forms bright yellow crystals, which are stable at the ordinary temperature, char on slowly heating, and explode slightly on rapid heating. Anthraquinone is precipitated on warming with acidified alcohol.

1:5-*Anthraquinonebisdiazonium hydrogen sulphate*,



from 1:5-diaminoanthraquinone, forms orange crystals, exploding slightly at about 172°.

Anthraquinone-1:5-bisazo-β-naphthol crystallises from nitrobenzene in small, green, metallic rods. The *α-naphthol* derivative crystallises well from phenylhydrazine.

The diazonium sulphates of 1:3- and 1:8-diaminoanthraquinone are much more readily soluble than the 1:5-derivatives. C. H. D.

Sulphur Dyes. PAUL FRIEDLÄNDER and FERD. MAUTHNER (*Zeit. Farb. Text. Ind.*, 1904, **3**, 333—337).—The following substances were prepared in order to test the view that the sulphur dyes may contain a disulphide group which, under the action of sodium sulphide, is resolved into the sulphydryl group, thus being rendered soluble.

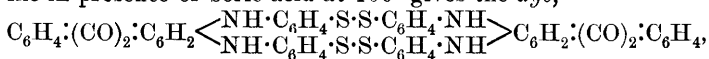
o-Chlorothiophenol, prepared by the reduction of *o*-chlorobenzenesulphonic chloride, boils at 205—206° and is easily oxidised to form *o*-dichlorodiphenyl sulphide, which crystallises from alcohol in needles and melts at 89—90°; the chlorothiophenol obtained by Otto (*Annalen*,

1868, 143, 109), which melts at 53—54°, is therefore not the ortho-compound, as usually assumed, but probably the para-derivative.

o-Dihydroxydiphenyl disulphide cannot readily be obtained from the foregoing *o*-chlorothiophenol, but is prepared from diazotised *o*-aminophenol by means of the xanthate reaction; as a by-product in this preparation, the substance, $C_6H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ O \end{smallmatrix} CS$, is formed by the loss of 1EtOH from the xanthate; it crystallises from alcohol in slightly yellow needles melting at 99·5°, and by alcoholic potassium hydroxide is converted quantitatively into thiocatechol, $OH \cdot C_6H_4 \cdot SH$.

The *azo*-compound, $S_2[C_6H_3(OH) \cdot N_2 \cdot C_{10}H_6 \cdot SO_3H]_2$, prepared by coupling *o*-dihydroxydiphenyl disulphide with diazotised naphthionic acid, dissolves in sodium sulphide solution giving a violet-coloured compound (the *azo*-derivative of the thiophenol), which is reoxidised in the air, regenerating the brownish-orange *azo*-derivative. A similar change of colour, indicating the formation of a sulphydryl group, occurs in the case of the compound of the same disulphide with diazotised benzidine.

The interaction of *o*-diaminodiphenyl disulphide with hydroquinazine in presence of boric acid at 100° gives the *dye*,



which crystallises from ethyl benzoate in long, dark blue needles and does not melt at 280°; it is not soluble in sodium sulphide solution.

W. A. D.

Preparation of Crystallised Proteids. MICHAEL COHN (*Zeit. physiol. Chem.*, 1904, 43, 41—43).—Crystallised ovalbumin can only be obtained from fresh eggs, otherwise it is obtained in an amorphous condition. The crystals are obtained by the addition of 10 per cent. acetic acid after the removal of globulins by means of ammonium sulphate. A second crop of crystals may be obtained by the further addition of acetic acid.

The best yields of crystallised serumalbumin are also obtained when fresh blood is employed. Some 10—14 c.c. of *N*/5 sulphuric acid are used for each 100 c.c. of liquid, and the crystallisation proceeds more rapidly on a warm than on a cold day. The product is pure only after several recrystallisations by solution in water and precipitation with ammonium sulphate.

The albumin does not become insoluble or amorphous under such treatment.

J. J. S.

Hydrolysis of the Liver Proteid. JULIUS WOHLGEMUTH (*Ber.*, 1904, 37, 4362—4364. Compare *Abstr.*, 1903, ii, 440; 1904, ii, 751).—The nucleoproteid of the liver on hydrolysis with sulphuric acid and subsequent removal of most of the products of hydrolysis by the ester method yielded a residue from which two *copper* salts were obtained. The one, $C_{10}H_{18}O_5N_2Cu$, insoluble in alcohol, yielded an acid, $C_{10}H_{20}O_5N_2$, probably a *diaminohydroxysebacic acid*; the other, $C_8H_{13}O_5NCu$, is soluble in alcohol.

E. F. A.

Deaminoalbumins. S. LEVITES (*Zeit. physiol. Chem.*, 1904, **43**, 202—206).—Deaminoalbumins have been obtained from egg-albumin, casein, and gelatin by Schiff's method (compare Abstr., 1896, i, 632; Paal, *ibid.*, i, 455). The deamino-compounds give both the biuret and Millon reactions, and are less rich in total nitrogen but slightly richer in amino-nitrogen than the substances from which they were obtained. This would indicate that the presence of acid amide, $\cdot\text{CO}\cdot\text{NH}_2$, groups in the original proteid molecules has not yet been established.

J. J. S.

Decomposition of Pseudomucin by Concentrated Boiling Acids. II. J. OTORI (*Zeit. physiol. Chem.*, 1904, **43**, 74—85. Compare Abstr., 1904, i, 1067).—The following products have been obtained by hydrolysing pseudomucin with hydrochloric acid and stannous chloride, according to Hlasiwetz and Habermann's directions (this Journal, 1872, 1069; 1874, 172). The numbers refer to parts per 100 parts of pseudomucin. Ammonia, 3.24; guanidine, 0.025; arginine, 0.777; lysine, 2.58; tyrosine, 0.44; leucine, 4.43; glycine, 0.146; glutamic acid, 0.594; valeric acid, 0.765; acetic (with a little propionic) acid, 0.161; humin, 7.005. Aspartic acid, formic acid, and a reducing sugar are also formed. The differences both as regards the nature and the amount of the products obtained, when sulphuric acid is used on the one hand, and hydrochloric acid and stannous chloride on the other, are accounted for first by the more energetic hydrolytic action of the hydrochloric acid, and secondly by the reducing properties of the stannous chloride.

Small amounts of guanidine have been isolated, in the form of guanidine cadmium chloride, from the products obtained by boiling casein and gelatin with hydrochloric acid.

It is pointed out that ether completely extracts stannous chloride from its aqueous solutions.

J. J. S.

Oxidation of Pseudomucin and of Casein with Calcium Permanganate. J. OTORI (*Zeit. physiol. Chem.*, 1904, **43**, 86—92).—Pseudomucin and casein have been oxidised by Zickgraf's method (Abstr., 1903, i, 666; 1904, i, 955), but in neither case did the maximum production of the guanidine (determined as picrate) coincide with the disappearance of the biuret reaction, although on the whole the amount of guanidine showed an increase as the biuret reaction became less marked. The sparingly soluble calcium compounds were worked up according to Kutscher and Schenck's method (Abstr., 1904, i, 955), and a compound subliming at about 260° was obtained from pseudomucin together with a compound melting and decomposing at 330° .

The calcium compound from casein gave oxamic acid or Zickgraf's compound.

J. J. S.

Caseinokyrine. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1904, **43**, 46—67).—Caseinokyrine is formed when casein is digested with 12 or 16 per cent. hydrochloric acid at 38 — 39° during three weeks, and may be isolated by means of phosphotungstic acid and purified by repeated crystallisation of its sulphate in order to free it from small

amounts of tyrosine. Pyrrolidine-2-carboxylic acid is also formed at the same time.

Caseinokyrine sulphate, $C_{23}H_{47}O_8N_9 \cdot 3H_2SO_4$, has not been obtained in a crystalline form, but the *phosphotungstate* crystallises in much the same manner as glutokyrine phosphotungstate.

Both caseinokyrine and glutokyrine give the biuret reaction. Mercuric sulphate yields a precipitate with caseinokyrine which dissolves on the addition of dilute sulphuric acid, and thus differs from histidine sulphate.

When hydrolysed by heating with 33 per cent. sulphuric acid for 12 hours, the chief products are arginine, lysine, and glutamic acid, but neither histidine nor glycine. The proportions are: basic nitrogen 84—85 per cent., and nitrogen as amino-acids 15—16 per cent. of the total nitrogen. These values agree fairly well with the assumption that caseinokyrine is derived from 1 molecule of arginine, 2 molecules of lysine, and 1 molecule of glutamic acid *minus* 2 molecules of water.

The caseinokyrine was carefully tested and shown to be free from arginine and lysine before hydrolysis. J. J. S.

Glutokyrine. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1904, 43, 44—45. Compare Abstr., 1903, i, 587).—Glycine is formed when glutokyrine is boiled with 33 per cent. sulphuric acid for 6 hours. Glutamic acid is also formed. J. J. S.

Preparation and Analysis of Nucleic Acids. VII. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1904, 43, 199—201. Compare Abstr., 1901, i, 623; 1903, i, 668, 779; 1904, i, 126, 955).—Lævulic acid has been detected among the products obtained by the hydrolysis with 25 per cent. sulphuric acid at 100° of the nucleic acids from spleen, pancreas, brain, and testicles. The acid was isolated as its silver salt, and not as its phenylhydrazone (compare Inouye, this vol., i, 837). J. J. S.

Cerebrone. HANS THIERFELDER (*Zeit. physiol. Chem.*, 1904, 43, 21—31. Compare Abstr., 1901, i, 176).—Cerebrone is identical with Gamgee's pseudo-cerebrin (*Text Book of Physiology*, 1880). The name cerebrone is retained. On hydrolysis with 7 per cent. sulphuric acid under pressure, it yields galactose, cerebroic acid, and Thudichum's sphingosine, $C_{17}H_{35}O_2N$.

The formation of galactose is complete after some four hours, and the amount is 20 per cent. of the cerebrone. *Cerebroic acid*, $C_{25}H_{50}O_3$, separates as a snow-white powder from alcohol, melts at 99° when slowly heated, yields a *sodium* salt, $C_{25}H_{49}O_3Na$, and an *acetyl* derivative which has only been obtained in the form of a gelatinous mass. The *sodium* salt of the acetyl derivative, $C_{25}H_{48}O_3AcNa$, has been prepared. J. J. S.

Compounds of Mesoporphyrin with Iron and Manganese. JEAN ZALESKI (*Zeit. physiol. Chem.*, 1904, 43, 11—17. Compare Abstr., 1903, i, 217, 375).—A solution of mesoporphyrin hydrochloride

in 80 per cent. acetic acid saturated with sodium chloride reacts with ferrous acetate solution yielding a crystalline product which in many respects resembles hæmin. The crystals are darker, thicker, and more pronouncedly triclinic in habit. It does not contain a methoxy-group, and, when heated with acetic acid saturated with hydrogen bromide, it yields mesoporphyrin hydrochloride. The compound does not dissolve in dilute acids or in concentrated hydrochloric acid. Its solutions in chloroform, ether, alcohol, or acetone are more strongly coloured than corresponding solutions of hæmin. It may be repeatedly crystallised from acetic acid without undergoing decomposition, and dissolves readily in dilute alkalis. The absorption spectrum of acetic acid solutions resembles that of hæmin, but the characteristic bands are somewhat nearer the violet end. It yields esters in exactly the same manner as hæmin. The *ethyl* ester forms rhombic crystals insoluble in alkalis, but readily soluble in chloroform, acetone, or ether.

When hæmatoporphyrin is used in place of mesoporphyrin, the product is hæmin, and not the new compound, which probably contains four atoms of hydrogen more in the molecule than hæmin, and it is therefore termed *hydrohæmin*; it has the composition $C_{34}H_{36}O_4N_4ClFe$.

A corresponding *manganese* compound has been obtained by using manganous acetate; it closely resembles the iron compound, but is more readily soluble in acetic acid, and has characteristic absorption band $\lambda 593-585$ and $\lambda 570-540$, and the right end of its spectrum from $\lambda 487$ is quite dark.

J. J. S.

Adrenaline and Alkylaminoacetylcatechol. FRIEDRICH STOLZ (*Ber.*, 1904, **37**, 4149—4154. Compare Abstr., 1904, i, 873, 1069, and Jowett, *Trans.*, 1904, **85**, 192).—*Tri-p-chlorobenzoyladrenaline*, $C_9H_{10}O_3N(CO \cdot C_6H_4Cl)_3$, forms an uncrystallisable varnish melting at about 75° , and dissolves readily in alcohol, ether, or benzene, but not in water or dilute acids or alkalis.

The author's results obtained by methylating and oxidising adrenaline are identical with those of Jowett (*loc. cit.*). Methyl iodide and methyl-alcoholic sodium hydroxide react with adrenaline to form vanillin. These reactions indicate the formula of adrenaline as being $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$, and it should therefore be possible to synthesise the base by reducing methylaminoacetylcatechol.

[With HANS MEYER (Marburg).]—The alkylaminoacetylcatechols (*Abstr.*, 1904, i, 873) and their reduction products have physiological properties closely resembling those of adrenaline.

Aminoacetylcatechol, $C_8H_9O_3N$, prepared by the action of ammonia on chloroacetylcatechol, forms a yellowish-white, crystalline powder, which darkens at 200° and decomposes slowly at about 300° . The *hydrochloride* crystallises from alcohol in colourless leaflets and melts and decomposes at 260° .

C. H. D.

Adrenaline. GABRIEL BERTRAND (*Bull. Soc. chim.*, 1904, [iii], **31**, 1289—1292. Compare Abstr., 1904, i, 956).—Adrenaline crystallises in small lamellæ joined together to form branches which are grouped

into spheres. The prismatic crystals seen in commercial preparations of this material are probably magnesium ammonium phosphate. It is soluble in water to the extent of 0.0268 per cent. at 20°, less than this in alcohol, and not at all in the other common organic solvents, but dissolves in acids and alkalis. A solution in decinormal sulphuric acid had $[\alpha]_D - 53.3^\circ$ (compare Pauly, *Abstr.*, 1904, i, 128, and Jowett, *Trans.*, 1904, 85, 192). Adrenaline melts on the Maquenne block at 263°.

T. A. H.

Action of Amino-acids on Amylase. JEAN EFFRONT (*Bull. Soc. chim.*, 1904, [iii], 31, 1230—1233. Compare *Abstr.*, 1893, i, 187).—The author finds that the accelerating influence of asparagine on the activity of amylase towards starch is due to the presence of the amino-group and not to that of the amide group, since aspartic acid, glycine, sarcosine, alanine, leucine, and glutamic and hippuric acids exert a similar accelerating action whereas succinamide, acetamide and its homologues, and benzamide exhibit a retarding influence, as do also the amines, hydroxylamine and hydrazine and their salts. This influence of the amino-acids has nothing in common with that due to organic acids, since glycine in presence of acetic acid shows a greater acceleration than the latter. This action would seem to indicate that the amino-acids exert a beneficial influence in the germination of starchy seeds, especially in the initial stages, when but little amylase is present.

T. A. H.

Studies on Enzyme Action: Effect of "Poisons" on the Rate of Decomposition of Hydrogen Peroxide by Hæmase. GEORGE SENTER (*Proc. Roy. Soc.*, 1904, 74, 201—217. Compare *Abstr.*, 1903, ii, 661).—The influence of various substances on the rate of decomposition of hydrogen peroxide by hæmase has been quantitatively studied. Acids markedly retard the decomposition, and their influence is in general proportional to the number of hydrogen ions they contain. Nitric acid, however, is more, and acetic acid is less, "poisonous" than would be expected from the hydrogen ions present. The length of time during which the acid is in contact with the enzyme before the peroxide is added is of no consequence. Further, if the acid is neutralised before the addition of the peroxide, the change takes place at the normal rate. With alkalis also, at least in stronger solutions, there is a retarding effect. The retardation, unlike that due to acids, depends on the period of incubation, but the normal velocity is observed if the alkali has been neutralised previous to the addition of peroxide. The influence of a large number of neutral salts on the rate of decomposition has been studied, without indicating much of a general character. Dilute solutions may have an accelerating influence, concentrated solutions of the same salt a retarding influence. The halogen derivatives of the alkalis and alkaline earths exert a considerable retarding influence, whilst sodium acetate accelerates the decomposition quite appreciably. Substances which have a markedly "poisonous" influence are hydrogen sulphide, hydroxylamine, mercuric chloride and bromide; formaldehyde, mercuric cyanide, carbon monoxide, iodine, and arsenious oxide have a very slight influence on the catalysis.

From the results obtained with acids and alkalis, it is concluded

that at least some enzymes are amphoteric substances. The author favours the view that the poisonous action of the above-mentioned substances is to be referred in most cases to a formation of compounds with the enzyme which are inactive towards hydrogen peroxide.

The solution of hæmase is to be regarded as a two-phase system, and there are therefore reasons for supposing that what is actually measured is the rate of diffusion of the hydrogen peroxide to the enzyme, the rate of actual decomposition of the peroxide by the enzyme being very great (compare Bodenstein, *Abstr.*, 1904, ii, 245; Nernst, *Abstr.*, 1904, ii, 315; Brunner, *ibid.*). J. C. P.

Ferments which Decompose Nuclein Compounds. ALFRED SCHITTENHELM (*Zeit. Physiol. Chem.*, 1904, 43, 228—239. Compare *Abstr.*, 1904, ii, 752; Jones and Partridge, *ibid.*, 838).—An active enzyme solution has been obtained by precipitating an aqueous extract of spleen with ammonium sulphate, suspending in water with a little chloroform, thoroughly shaking, dialysing, and filtering. Such a solution readily transforms guanine into uric acid when air is passed through the solution, but in the absence of air xanthine is produced. The solution has not the power of hydrolysing nucleic acids to purine bases and then of transforming these into uric acid. The author is of opinion that three distinct ferments take part in the transformation of nucleic acids into uric acid, namely: 1. A *nuclease* which hydrolyses the nucleic acid to purine bases. This enzyme is present in the spleen extract, but not in the solution of the precipitated enzyme. 2. An enzyme *guanase* or *adenase* which has deamidising functions and transforms guanine into xanthine and adenine into hypoxanthine. This enzyme appears to be extremely widely distributed in the animal tissues. 3. An oxidising enzyme, which, in the presence of air, converts hypoxanthine into xanthine and this into uric acid. The last enzyme is not so widely distributed and is localised in certain special organs.

The precipitation of the spleen extract with alcohol yields a product which is not nearly so active as that obtained by precipitating with ammonium sulphate.

Enzymes which are capable of destroying uric acid are also present in spleen and nerve extracts (compare Ascoli, *Pflüger's Archiv*, 1898, 72, 340). J. J. S.

Saponification of Cocoa Nut Oil by Cytoplasm. EDOUARD URBAIN, L. SAUGON, and A. FEIGE (*Bull. Soc. chim.*, 1904, [iii], 31, 1194—1198).—Cocoa nut oil is saponified by Nicloux's cytoplasm (*Abstr.*, 1904, ii, 508), but the action is retarded by the fatty acid, and the retarding influence of the free acid is greater the lower its molecular weight. The saponification of the various glycerides in the oil by cytoplasm appears to proceed at the same rate, and Connstein, Hoyer, and Wartenburg's results (*Abstr.*, 1903, ii, 218), which indicate the contrary, were probably due to the retarding influence of the butyric acid liberated in their experiments on the action of cytoplasm on tributyrin. T. A. H.

Organic Chemistry.

Fundamental Conceptions underlying the Chemistry of the Element Carbon. JOHN U. NEF (*J. Amer. Chem. Soc.*, 1904, **26**, 1549—1577).—The fundamental conceptions on which the present system of organic chemistry is based are the constant quadrivalence of carbon and the process of substitution. These conceptions are discussed in the light of recent work, and it is pointed out that they are inadequate, and must be replaced by the conceptions of a variable carbon valency and of dissociation in its broadest sense. The importance of the so-called methylene chemistry is insisted on. It is suggested that at certain temperatures, which vary according to the nature of the groups or atoms united to it, the quadrivalent carbon atom spontaneously becomes bivalent, whilst at lower temperatures the bivalent and quadrivalent carbon atoms are in dynamic equilibrium. The mechanism of substitution must be regarded as the union of an unsaturated molecule with a second molecule to form an additive compound which in many cases subsequently dissociates spontaneously with formation of two new molecules. E. G.

isoHexanes in Roumanian Petroleum. PETRUS PONI and N. COSTACHESCO (*Ann. Sci. Univ. Jassy*, 1904, **3**, 95—102. Compare Abstr., 1903, i, 593).—The nature of the hexanes in the fraction of petroleum from Colibasi distilling between 58° and 66° has been investigated. This fraction was twice refractionated, and the fraction obtained at 61·5—62·5° was treated with nitric acid of sp. gr. 1·4 in a sealed tube at a temperature of 60°.

The nitrated product was dried and fractionated under a pressure of 35 mm. More than half distilled at 75—76°. From the sp. gr. (0·9681 at 0°/0°) and the boiling point (168—170° under 750 mm.), this appears to be γ -nitro- γ -methylpentane.

The fraction of highest boiling point (150—158°) is a dinitro-compound, but it was only obtained in very small quantity. At intermediate temperatures, mixtures of mono- and di-nitro-derivatives were obtained. The hydrocarbon unattacked by the nitric acid is β -methylpentane. The same products were obtained by treating the fractions collected at 59·5—61·5° and 63·5—64·5° in the same manner, and the results indicate that the petroleum fraction examined consists essentially of a mixture of β -methylpentane and γ -methylpentane.

When treated with fuming nitric acid of sp. gr. 1·525, two crystalline products are obtained. One of these is identical with $\beta\gamma\gamma$ -trinitro- β -methylpentane. The other forms acicular crystals melting at 85° and appears to be $\beta\beta\gamma$ -trinitro- γ -methylpentane (compare Young, *Trans.*, 1898, **73**, 930). Oxalic acid and carbon dioxide were the only oxidation products observed in the action of the nitric acid of sp. gr. 1·4; carbon dioxide alone being formed in the action of the fuming acid. H. M. D.

Preparation of Acetylene Tetrachloride. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 154657. Compare Berthelot and Jungfleisch, 1870).—Acetylene tetrachloride is best prepared by passing acetylene and chlorine alternately into antimony pentachloride and fractionally distilling the product. The gases may also be passed in simultaneously if precautions are taken to prevent contact between the two gases and to prevent supersaturation at any point.

C. H. D.

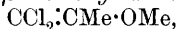
Trichloroisopropyl Alcohol. EDOUARD VITORIA (*Bull. Acad. Roy. Belg.*, 1904, 1087—1123. Compare Abstr., 1904, i, 279 and 794).— $\gamma\gamma\gamma$ -Trichloroisopropyl alcohol, $\text{CCl}_3\cdot\text{CHMe}\cdot\text{OH}$, prepared as already described (*loc. cit.*), forms monoclinic crystals similar to those of potassium tetrathionate (the crystallographic measurements are given in the original). It exerts vapour pressures equivalent to 3, 18, and 115 mm. of mercury at 19° , 56° , and 100° respectively. The alcohol could not be deracemised.

$\gamma\gamma\gamma$ -Trichloroisopropyl acetate is a colourless liquid with an odour recalling that of ethyl acetate; it melts at 8° , boils at 180 — 181° under 766 mm. pressure, has a sp. gr. 1.353 at $15^\circ/15^\circ$ and n_D 1.46017. The nitrate is a colourless or slightly yellow liquid having a sp. gr. 1.499 at 13° and n_D 1.47982. Attempts to prepare the benzoate, chloride, and bromide by the usual methods were unsuccessful.

When treated with phosphoric oxide, trichloroisopropyl alcohol furnishes the corresponding $\gamma\gamma\gamma$ -trichloropropylene, $\text{CCl}_3\cdot\text{CH}\cdot\text{CH}_2$, which is a colourless, mobile liquid with an odour like that of aldehyde; it melts at -30° , boils at 114 — 115° under 757 mm. pressure, has a sp. gr. 1.359 at 13° , and readily combines with chlorine to form pentachloropropane, $\text{CCl}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$; this crystallises from warm alcohol in colourless needles, has a camphoraceous odour, and melts at 179 — 180° . $\gamma\gamma\gamma$ -Trichloro- $\alpha\beta$ -dibromopropane, $\text{CCl}_3\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, similarly prepared, melts and decomposes slightly at 210° , but in other respects resembles the pentachloropropane.

On oxidation with chromic acid, trichloroisopropyl alcohol gave negative results, but with nitric acid some trichloroacetic acid was produced. These results indicate that the alcoholic character of the substance and the reactivity of the H atom in the group $-\text{CH}\cdot\text{OH}$ are enfeebled by the presence of the three chlorine atoms.

In attempting to prepare various ethers from $\gamma\gamma\gamma$ -trichloroisopropyl alcohol by the application of the Grignard reaction to tetrachloro-ethers of the type $\text{CCl}_3\cdot\text{CHCl}\cdot\text{OR}$, a series of alkoxydichloropropylenes was obtained. β -Methoxy- $\alpha\alpha$ -dichloropropylene,



is a colourless liquid, which melts at -71° or -72° , boils at 126 — 127° under 750 mm. pressure, has a sp. gr. 1.239 at 20° and n_D 1.469. β -Ethoxy- $\alpha\alpha$ -dichloropropylene melts at -80° to -85° , boils at 144 — 146° under 763 mm. pressure, has a sp. gr. 1.179 at 20° and n_D 1.46434. β -Propoxy- $\alpha\alpha$ -dichloropropylene melts at -90° , boils at 163 — 164° under 764 mm. pressure, has a sp. gr. 1.134 at 20° and n_D 1.45939. All these derivatives readily combine with halogens.

Chloral propyl alcoholate, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OPr}^a$, is liquid, and with

phosphorus pentachloride yields the *tetrachloro-ether*, $\text{CCl}_3 \cdot \text{CHCl} \cdot \text{OPr}^a$, which boils at 199—200° under 764 mm. pressure. T. A. H.

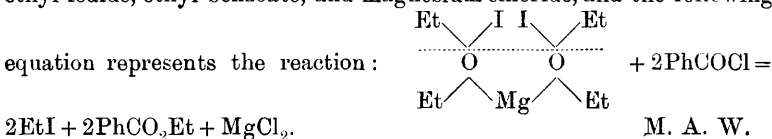
Action of Organomagnesium Compounds on β -Hydroxy-aldehydes and on Keto-alcohols. ADOLF FRANKE and MORITZ KOHN (*Ber.*, 1904, **37**, 4730—4731. Compare Abstr., 1904, i, 845).—A good yield of *pentane- $\beta\delta$ -diol*, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$, may be obtained by the action of magnesium methyl iodide (2 mols.) on aldol; it is a viscid, colourless liquid, distils at 98° under 12 mm. pressure or at 198—199° under 748 mm. The *diacetate* distils at 88° under 10.5 mm., or at 200—202° under the ordinary pressure.

Diacetonealcohol and magnesium methyl iodide yield *$\beta\delta$ -dimethyl-pentane- $\beta\delta$ -diol*, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OH}$, which is also a viscid liquid with a faint odour of peppermint. It distils at 98° under 13 mm. pressure.

Formylisobutyrylaldol and magnesium ethyl iodide yield, in addition to the hydroxypivalic ester already described (*loc. cit.*), a *glycol*, probably *$\beta\beta$ -dimethylpentane- $\alpha\gamma$ -diol*, $\text{OH} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Me}$, which melts at 55° and distils at 211—214°. J. J. S.

Quadrivalent Oxygen. EDMOND E. BLAISE (*Compt. rend.*, 1904, **139**, 1211—1213).—The crystalline compound melting at 52--53°, obtained by the action of magnesium on iodine in the presence of ether, probably has the constitution $\text{OEt}_2 \left\langle \begin{smallmatrix} \text{I} & \text{I} \\ & \text{Mg} \end{smallmatrix} \right\rangle \text{OEt}_2$ (compare Abstr., 1901, i, 317, and Zelinsky, Abstr., 1903, i, 802), and similar compounds are obtained when the ethyl ether in the above reaction is replaced by methyl amyl ether or by phenyl amyl ether, but the products are not crystalline, whilst diethyl methylene ether or ethyl acetate yield the solid compounds $\text{Mg}(\text{OEtI} \cdot \text{CH}_2 \cdot \text{OEt})_2$ and $\text{MgI}_2 \cdot 6\text{MeCO}_2\text{Et}$ respectively. The basic character of the quadrivalent oxygen in these compounds increases with the complexity of the alkyl groups associated with them; thus, the ethyl ether in the compound of magnesium iodide and ethyl ether is readily replaced by amyl ether, diethyl methylene ether, or by ethyl acetate, and less readily by methyl amyl ether, whilst ethyl ether readily replaces the more acidic phenyl ethyl ether in the compound it forms with magnesium iodide.

Direct evidence in favour of the constitution suggested for the compound of magnesium iodide and ether is afforded by the action of benzoyl chloride at the temperature of boiling water; the products are ethyl iodide, ethyl benzoate, and magnesium chloride, and the following



Electrolysis of Potassium Acetate. FRITZ FOERSTER and A. FIGUET (*Zeit. Elektrochem.*, 1904, **10**, 924—925).—In reply to the criticisms of Hofer and Moest (this vol., i, 8) of the authors' previous paper on this subject (Abstr., 1904, i, 965), they point out that the fact

that they mistook the nature of the reaction brought about by that portion of the current which does not produce ethane does not affect the accuracy of their determinations of the division of the current between ethane-forming and non-ethane-forming reactions. T. E.

Constitution of Sodium Salts of Certain Acids containing a Methylene or Methinene Grouping. Alkyl Cyanoacetates, Acylcyanoacetates, Malonates, and Cyanomalonates; Malononitrile and Cyanocamphor. ALBIN HALLER and PAUL T. MULLER (*Compt. rend.*, 1904, 139, 1180—1185. Compare Abstr., 1904, ii, 221).—It has already been shown by one of the authors (Muller, 1902, i, 354; Muller and Bauer, 1903, ii, 705) that the difference between the molecular refraction for the *D* ray of a normal acid and its sodium salt is less than 2 (1·4 to 1·9), whilst the corresponding value in the case of a *pseudo*-acid is greater than 2. In the present paper, the densities and specific refractions for the α , γ , and *D* rays of solutions of approximately equal concentration in absolute alcohol of acids containing a methylene or methinene grouping and their sodium salts are given; the difference between the molecular refraction for the *D* ray of the acid and its salt is in all cases greater than 2, and the following table comprises the results:

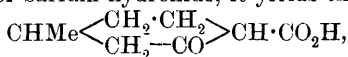
Acid.	M_p		Diff.
	Salt.	Acid.	
Ethyl cyanoacetate	33·03	26·84	6·19
Ethyl cyanomalonate	49·48	44·23	5·25
Ethyl cyanopropionylacetate	46·73	44·00	2·73
Ethyl malonate	42·00	38·10	3·90
Malononitrile	21·21	15·67	5·54
Cyanocamphor	54·93	49·18	5·75

Whence it follows that the acids are *pseudo*-acids, that is, the acid and its salts have different chemical constitutions. M. A. W.

Action of Ethyl Sodioacetoacetate on Dibromo-hydrocarbons. ANDREI A. SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 947—988 and 1209—1244).—After discussing the results obtained by other investigators in this direction, the author gives his own results, which are briefly as follows.

With $\alpha\gamma$ -dibromobutane, ethyl sodioacetoacetate gives, together with small quantities of acetic and dehydracetic acids, mainly the ester $\text{CHMe} \begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{CHAc}\cdot\text{CO} \end{smallmatrix} \text{CH}\cdot\text{CO}_2\text{Et}$, which separates in very large prisms, melting at 34° and boiling at 116—118° under 16 mm. pressure; it is readily soluble in alcohol, ether, light petroleum, benzene, or chloroform, and it does not decolorise cold 2 per cent. potassium permanganate solution; sulphuric acid is not coloured by it in the cold, but nitric acid rapidly turns it green; with vanillin and concentrated hydrochloric acid, it gives after some time a red coloration, which is rapidly changed to emerald-green by heating; it gives a liquid compound with phenylhydrazine and only combines with semicarbazide on heating.

Under the action of barium hydroxide, it yields the acid

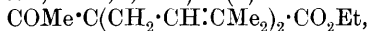


melting at 125—126° (compare Buchner, Abstr., 1898, i, 639); the *silver* salt of this acid was prepared and analysed.

With $\alpha\beta$ -dibromo- β -methylpropane, ethyl sodioacetoacetate gives mainly α -bromo- β -methylpropylene and *isobutylene*.

With ψ -butylene bromide (β -butylene bromide), it yields the two stereoisomeric β -bromo- Δ^2 -butylenes.

With $\beta\delta$ -dibromo- β -methylbutane, ethyl sodioacetoacetate yields: (1) a small proportion of ethyl dimethylallyl ether, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OEt}$, but mainly the two following compounds. (2) Ethyl $\delta\delta$ -dimethylallyl-acetoacetate (compare Ipatieff, Abstr., 1901, i, 256), which refractometric and magnetic polarisation measurements show to have the enolic structure, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})\text{:CMe}\cdot\text{OH}$. Heating the ester with barium hydroxide solution gives principally the methylheptenone, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, together with a small quantity of the methylhexenoic acid prepared by Barbier (*Bull. Soc. chim.*, 1887, [ii], 47, 701) and by Léser (Abstr., 1899, i, 414) and already studied by the author (Abstr., 1902, i, 256). (3) The *ester*



which boils at 140—149° under 13 mm. pressure and at 280—290° under the ordinary pressure; on heating with barium hydroxide solution, it gives the *ketone* $\text{COMe}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_2)_2$, which boils at 230°, and the *acid* $\text{CH}(\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_2)_2\cdot\text{CO}_2\text{H}$, boiling at 121—131° under 13 mm. pressure, the *silver* salt of which was prepared.

With $\beta\gamma$ -dibromo- β -methylbutane, ethyl sodioacetoacetate gives principally α -bromo- α -methyl- Δ^2 -butylene.

With $\beta\delta$ -dibromopentane, ethyl sodioacetoacetate yields mainly the *ester* $\text{CMe}_2\text{:CH}\cdot\text{CHMe}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, which boils at 120—125° under 18 mm. pressure and at 234—238° under ordinary pressure, and has the sp. gr. 0.99395 at 0°/0° and 0.97712 at 19°/0°; the enolic formula is indicated by refractometric and magnetic rotation measurements. When boiled with barium hydroxide solution, it undergoes principally the ketonic decomposition, yielding the *ketone*



which boils at 178—189°, has the sp. gr. 0.87030 at 0°/0° and 0.85404 at 19.4°/0°, and forms a *semicarbazone*, $\text{C}_{10}\text{H}_{19}\text{ON}_3$, melting at 140°; the ketone is accompanied by a small quantity of the acid $\text{CMe}_2\text{:CH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, the silver salt of which was prepared and analysed.

With $\beta\epsilon$ -dibromohexane, ethyl sodioacetoacetate gives (1) the *ester* $\begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\cdot\text{CHMe} \end{array} > \text{CAc}\cdot\text{CO}_2\text{Et}$, which boils at 125—130° and has the sp. gr. 1.0617 at 0°/0° and 1.0457 at 19.2°/0°; (2) the *ester* $\text{C}_2\text{H}_4(\text{CHMe}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et})_2$, boiling at 120—125°.

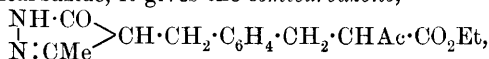
With $\alpha\gamma$ -dibromo- γ -ethylpentane, ethyl sodioacetoacetate yields mainly the unsaturated *ester*, $\text{CEt}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, which boils at 142—147° under 14 mm. pressure and has the sp. gr. 0.9854 at 0°/0° and 0.9713 at 16.8°/0°. When heated with barium hydroxide, the ester gives mainly ketone with a small proportion of acid.

With *p*-xylylene dibromide, ethyl sodioacetoacetate gives exclusively the ester $C_6H_4(CH_2 \cdot CHAc \cdot CO_2Et)_2$, which is deposited from alcohol in crystals melting at 62.5° . When heated with barium hydroxide or dilute potassium hydroxide solution, this yields: (1) the compound $C_6H_4(CH_2 \cdot CH_2Ac)_2$, which crystallises from alcohol in shining plates melting at $53-54^\circ$ and is readily soluble in benzene or ether; (2) the acid $CH_2Ac \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot CHAc \cdot CO_2H$, separating from water in crystals melting at 206° ; the silver salt was prepared and analysed; (3) small quantities of acetic, dehydracetic, and an unknown acid.

With *o*-xylylene dibromide, ethyl sodioacetoacetate gives: (1) the ester $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CAc} \cdot CO_2Et$, which boils at $185-190^\circ$ under 21 mm. pressure and has the sp. gr. 1.122666 at $0^\circ/0^\circ$ and 1.106205 at $19.2^\circ/0^\circ$, and n_D 1.51144 at 19.2° . When heated with barium hydroxide solution, it yields (a) the compound, $C_6H_4:(CH_2)_2 \cdot CHAc$, which boils at $164-168^\circ$ under 47 mm. pressure, has the sp. gr. 1.0685 at $0^\circ/0^\circ$ and 1.0546 at $17.5^\circ/0^\circ$, and n_D 1.53320 at 22° ; the semicarbazone, $C_{12}H_{15}ON_3$, of this methyl hydrindeneketone separates from alcohol in white, silky needles melting at about 178° ; (b) *o*-hydrindonaphthene-carboxylic acid (Perkin and Révay, Trans., 1894, 65, 228); (2) the ester, $C_6H_4(CH_2 \cdot CHAc \cdot CO_2Et)_2$, which boils at $222-256^\circ$ under 20-23 mm. pressure.

With *m*-xylylene dibromide, ethyl sodioacetoacetate yields the ester, $C_6H_4(CH_2 \cdot CHAc \cdot CO_2Et)_2$, which boils at $251-255^\circ$ under 58-60 mm. pressure, has the sp. gr. 1.107871 at $0^\circ/0^\circ$ and 1.09385 at $16.8^\circ/0^\circ$, and n_D 1.495256 at 19.7° .

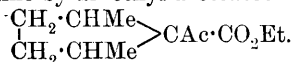
With semicarbazide, it gives the semicarbazone,



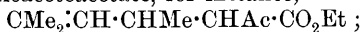
which separates from water in crystals melting and decomposing at 230° , and is soluble in ethyl or amyl alcohol, ether, ethyl acetate, or *m*-xylene. When heated with barium hydroxide solution, the ester yields: (1) the ketone, $C_6H_4(CH_2 \cdot CHAc)_2$, melting at $202-207^\circ$ under 23 mm. pressure and giving a semicarbazone, $C_{16}H_{24}O_2N_6$, melting and decomposing at 184° ; (2) *m*-phenylenedipropionic acid.

Concerning the action of ethyl sodioacetoacetate on dibromoderivatives of hydrocarbons, the following conclusions are drawn: (1) if the atoms of bromide in a dibromide with an open chain are not attached to neighbouring carbon atoms, products of combination of ethyl acetoacetate are always formed; if one bromine atom is tertiary and the other primary or secondary, unsaturated compounds with one or two double linkings are obtained; in the absence of a tertiary bromine atom, unsaturated acetoacetic esters are not formed, but esters of keto-acids with a polymethylene ring or else diacetoacetic esters; finally, condensation may occur and give rise to esters of keto-acids with a keto-polymethylene ring. (2) If the two atoms of bromine in a dibromide having an open chain are attached to two neighbouring carbon atoms, the compound does not combine with ethyl acetoacetate unless it contains one primary bromine atom. (3) When the bromine atoms are situated in a benzene or anthracene ring, no combination takes place with ethyl acetoacetate. (4) When

the bromine atoms are in side-chains of aromatic compounds, the reaction proceeds just as with aliphatic dibromo-compounds, and if the bromine atoms are in side-chains having the *o*-position to one another, the ring is simply closed, whilst where the side-chains are in the meta- or para-positions products are always obtained containing two acetoacetic residues. (6) All the products of combination of ethyl acetoacetate, obtained by the action of ethyl sodioacetoacetate on dibromides, may be ranged in the three following classes: (I) esters of β -keto-acids containing a polymethylene ring, formed by the replacement of two atoms of bromine by an ethyl acetoacetate residue, such as



(II) Unsaturated esters of β -keto-acids, divisible into two groups: (a) those containing one double bond in the radicle, formed after the action of ethyl sodioacetoacetate, for instance,



(b) those containing two double bonds in the radicle, formed after the action of ethyl sodioacetoacetate, for instance,



(III) Esters of keto-acids containing two ethyl acetoacetate residues and divisible into two classes: (a) diacetoacetic esters, such as $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{CHAc} \cdot \text{CO}_2 \text{Et})_2$; (b) keto-polymethylene esters of keto-

acids, such as $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CHAc} \cdot \text{CO} - \text{CH} \cdot \text{CO}_2 \text{Et} \end{array}$ T. H. P.

The Reduction of the Anhydrides of Dibasic Acids. GUSTAVE BLANC (*Compt. rend.*, 1904, **139**, 1213—1214).—When the anhydride of an unsymmetrical dibasic acid of the type $\text{CH}_2 \begin{array}{c} \text{CRR}' \cdot \text{CO} \\ \text{CH}_2 - \text{CO} \end{array} \text{O}$ was reduced by sodium and absolute alcohol (compare Bouveault and Blanc, *Abstr.*, 1903, i, 597, 673, 730; 1904, i, 213), a yield of 20—50 per cent. of the lactone, $\text{CH}_2 \begin{array}{c} \text{CRR}' \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{O}$, was obtained, and normal results were obtained with the anhydrides of pyrotartaric, $\alpha\alpha$ -dimethylsuccinic, $\alpha\alpha$ -dimethylglutaric, $\beta\beta$ -dimethylglutaric, and camphoric acids. *iso*-Propylsuccinic anhydride yielded a lactone which, on treatment with potassium cyanide and subsequent hydrolysis, gave a mixture of α - and β -isopropylglutaric acids, in which the latter preponderated.

M. A. W.

Solubility of Metallic Succinates in Water. H. CANTONI and D. DIOTALEVI (*Bull. Soc. chim.*, 1905, [iii], **33**, 27—36).—The solubilities of barium, strontium, calcium, copper and lead succinates in water at temperatures ranging from 0—50° have been determined, and in the cases of the alkaline earth metals compared with those of the malonates and oxalates. The results, which are given in tabular form in the original, show that the solubility of barium succinate slowly increases between 0° and 20° and then diminishes; that of strontium increases from 0—30°, then diminishes between 30° and 40°, and beyond this temperature again increases. Those of the calcium and lead salts increase

steadily with rise of temperature, whilst that of copper succinate increases until the temperature reaches 39° and then diminishes. It is suggested that the alternating changes in the case of the strontium salt are due to changes in the state of hydration and in that of the barium salt to polymorphism.

At 20° , the solubility of the three alkaline earth succinates decreases in the order strontium, barium, calcium, and at 40° in the order barium, strontium, calcium.

T. A. H.

Modes of Formation and Preparation of Aliphatic Aldehydes and a General Synthetical Method for the Preparation of Aldehydes. LOUIS BOUVEAULT (*Bull. Soc. chim.*, 1904, [iii], 31, 1306—1322, 1322—1327).—The first paper is a *résumé* of methods which have been devised from time to time for the preparation of aldehydes. The second paper deals in greater detail with the process already described by the author (Abstr., 1904, i, 13), which consists in gradually adding disubstituted formamides dissolved in dry ether to magnesium alkyl haloids (compare Beis, Abstr., 1904, i, 15, and Bodroux, *ibid.*, i, 421). The best yields are obtained when diethylformamide is employed. In addition to the aldehydes, other secondary products are formed in the reaction, in particular paraffins, produced by combination of two alkyl groups of the magnesium alkyl haloid employed. When dimethylformamide reacts with magnesium *iso*amyl chloride, there is formed as a by-product *dimethylaminodiamylmethane* [ζ -*dimethylaminoundecane*], $\text{CH}(\text{C}_3\text{H}_{11})_2 \cdot \text{NMe}_2$, a liquid having a characteristic amine-like odour and boiling at 110° under 15 mm. pressure and giving a *picrate* which is crystalline and melts at 103° .

The primary and secondary alkyl haloids react normally both in the Grignard reaction and in the subsequent interaction with formamides, but the magnesium derivatives of the tertiary haloids behave differently. The base formed together with amylene by the interaction of magnesium *tert.*-amyl chloride and diethylformamide (Abstr., 1904, i, 546) is probably produced in the manner indicated by the following scheme: $2\text{CMe}_2\text{Et} \cdot \text{MgCl} + \text{H} \cdot \text{CO} \cdot \text{NEt}_2 = \text{MgO} + \text{MgCl}_2 + \text{NEt}_2 \cdot \text{CH}(\text{CMe}_2\text{Et})_2 = \text{CMe}_2\text{Et} \cdot \text{CH}_2 \cdot \text{NEt}_2 + \text{CMe}_2 \cdot \text{CHMe}$. A number of aldehydes prepared by this process are referred to in the original.

T. A. H.

General Method of Synthesising Aldehydes by means of the Substituted Glycidic Acids. GEORGES DARZENS (*Compt. rend.*, 1904, 139, 1214—1217).—The ethyl esters of the disubstituted glycidic acids, readily prepared by the condensation of the corresponding ketone and ethyl chloroacetate in the presence of sodium ethoxide

according to the equation $\text{CORR}' + \text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Et} = \text{O} < \begin{matrix} \text{CRR}' \\ \text{CH} \cdot \text{CO}_2\text{Et} \end{matrix} +$

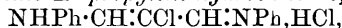
HCl , are colourless, odourless liquids boiling 60 — 70° higher than the corresponding ketones and not reacting with bromine, hydroxylamine, phenylhydrazine, or phenylurethane. The disubstituted glycidic acids obtained by hydrolysing the esters are unstable and readily break down into carbon dioxide and the corresponding aldehyde according to the equation $\text{O} < \begin{matrix} \text{CRR}' \\ \text{CH} \cdot \text{CO}_2\text{H} \end{matrix} =$

CHRR'·COH + CO₂. The boiling points of the ethyl disubstituted glycidates and the aldehydes thus prepared and the melting points of the semicarbazide of the latter are given in the following table :

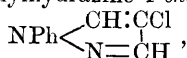
Ketone.	Boiling point of corresponding ethyl glycidate.	Boiling point of aldehyde.	Melting point of semi- carbazide.
	pressure.	pressure.	
Acetone	163-168° under 760 mm.	—	—
Methyl <i>isohexyl</i> ketone	151-152 „ 30 „	90° under 40 mm.	60°
Methyl heptyl ketone .	155-156 „ 19 „	105-106 „ 20 „	66-67
Methyl nonyl ketone...	165-170 „ 16 „	119-122 „ 16 „	85
Acetophenone.....	153-159 „ 20 „	95-97 „ 19 „	153-154
Tolyl methyl ketone...	160-164 „ 16 „	107-108 „ 19 „	159-160
<i>p</i> -Ethyl acetophenone..	210-215 „ 19 „	118-120 „ 20 „	—
Benzylacetone ...	175-180 „ 16 „	129-130 „ 19 „	70-72
Phenyl propyl ketone..	155-158 „ 18 „	122-123 „ 28 „	115-116
<i>iso</i> Butylacetophenone .	175-180 „ 16 „	153 „ 30 „	185-186
Methylcyclohexanone .	131-132 „ 15 „	66-67 „ 16 „	138-139

M. A. W.

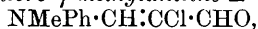
Chloromalonaldehyde [β -Chloro- Δ^{β} -propene- γ -ol- α -al]. WALTER DIECKMANN and LUDWIG PLATZ (*Ber.*, 1904, **37**, 4638—4646)— β -Chloro- γ -anilino- α -phenylimino- Δ^{β} -propylene hydrochloride,



obtained by heating mucochloric acid (Simonis, *Abstr.*, 1901, i, 268) with alcoholic aniline, crystallises from alcohol with 1EtOH in golden-yellow needles, and melts and decomposes at 228°; on adding it to an excess of boiling water, β -chloro- γ -anilino- Δ^{β} -propene- α -al (mono-anilide of chloromalonaldehyde), $\text{NPh}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CHO}$, is obtained in long, nearly colourless needles; it melts and decomposes at 193° and is hydrolysed by 30 per cent. aqueous potassium hydroxide giving chloromalonaldehyde, $\text{OH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CHO}$, which crystallises from chloroform in slender, colourless needles, melts and decomposes at 144°, readily reduces Fehling's solution, and gives, on dissolution in the aqueous alkali hydroxides, crystalline *sodium* and *potassium* derivatives. Aniline converts the aldehyde into the mono- and di-anilides just described, and with phenylhydrazine 4-chloro-1-phenylpyrazole,



is obtained; it crystallises from dilute alcohol in colourless needles and melts at 75°. β -Chloro- γ -methylanilino- Δ^{β} -propene- α -al,



prepared by the action of methylaniline on chloromalonaldehyde in alcoholic solution, forms colourless crystals and melts at 76°. The *benzoate*, $\text{CHO}\cdot\text{CCl}\cdot\text{CH}\cdot\text{OBz}$, of chloromalonaldehyde forms colourless needles and melts at 105°.

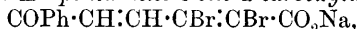
β -Bromo- γ -anilino- α -phenylimino- Δ^{β} -propylene hydrobromide,



obtained from mucobromic acid and aniline, crystallises from alcohol in golden needles and melts and decomposes at 217°. β -Bromo- γ -anilino- Δ^{β} -propene- α -al crystallises from alcohol in colourless needles,

melts and decomposes at 184° , and is easily convertible into bromomalonaldehyde, which has already been described by Lespieau (Abstr., 1902, i, 13). 4-Bromo-1-phenylpyrazole crystallises from alcohol in colourless needles and melts and decomposes at 81° .

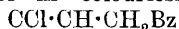
Incidentally the following substances are described. *Sodium* $\alpha\beta$ -dibromo- ϵ -phenyl- $\Delta^{\alpha\gamma}$ -pentadiene- ϵ -one- α -carboxylate,



obtained by the condensation of acetophenone and mucobromic acid, forms colourless crystals and decomposes at 154° . The lactone, $\text{CBr}\cdot\text{CH}\cdot\text{CH}_2\text{Bz}$

$\parallel \begin{matrix} > \text{O} \\ \text{CBr}\cdot\text{CO} \end{matrix}$, of $\alpha\beta$ -dibromo- ϵ -phenyl- Δ^{α} -pentene- γ -ol- ϵ -one- α -carb-

oxylic acid crystallises from alcohol in colourless leaflets and



melts at 168° . The analogous lactone, $\parallel \begin{matrix} > \text{O} \\ \text{CCl}\cdot\text{CO} \end{matrix}$, is similar and

melts at 121 — 122° .

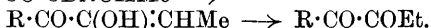
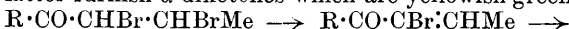
W. A. D.

Migration of the Ethylenic Linking in Alkyl Allyl Ketones.

EDMOND E. BLAISE (*Bull. Soc. chim.*, 1905, [iii], 33, 43—49. Compare Abstr., 1904, i, 290).—When alkyl allyl ketones are treated with hydrogen bromide even at -80° , they are converted into saturated bromo-ketones which, on treatment with potassium hydrogen carbonate, furnish alkyl propenyl ketones isomeric with the original alkyl allyl ketones, indicating that in these circumstances the ethylenic linking migrates from the $\alpha\beta$ - to the $\beta\gamma$ -position.

A similar change is brought about directly by boiling the ketones with dilute sulphuric acid (20 per cent.); the yield of the isomeride in this case is from 60—70 per cent., the loss being due partly to hydration of the ketone and partly to polymerisation. With sodium ethoxide, the alkyl allyl ketones furnish the corresponding ethoxyketones, thus ethyl allyl ketone under these conditions yields ethyl β -ethoxypropyl ketone. Further, when propyl allyl ketone (2 mols.) is boiled with formaldehyde (1 mol.) in presence of piperidine, no condensation occurs, but propyl propenyl ketone is formed.

The bromides of the alkyl allyl ketones are readily distinguished from their isomerides by ebullition with an aqueous solution of an alkali carbonate, the former yielding a colourless distillate, whereas the latter furnish α -diketones which are yellowish-green, thus:



The interaction with semicarbazide also serves to distinguish these two classes of unsaturated ketones, the alkyl allyl ketones furnishing under all conditions semicarbazones, whereas their isomerides furnish, with 1 mol. of semicarbazide, semicarbazones, and with 2 mols. of the reagent, semicarbazide-semicarbazones; the propenyl ketones also behave in the same way with hydroxylamine. The *semicarbazones* of methyl-, ethyl-, and propyl-propenyl ketones melt at 114° , 157° , and 147° respectively. A specimen of *ethyl semicarbazopropyl ketone semicarbazone*, $\text{CHMe}(\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}(\text{Et})\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which could not be obtained pure, melted at 157° . The hydroxylamino-

oxime derived from the same ketone is liquid, as is also its benzoyl derivative (compare Rupe and Schlochoff, *Abstr.*, 1904, i, 144).

T. A. H.

Constitution of Cellulose. CHARLES F. CROSS and EDWARD J. BEVAN (*Zeit. Farb. Text. Ind.*, 1904, 3, 441—442).—A reply to Green (this vol., i, 22).

W. A. D.

Humic Acid. PH. MALKOMESIUS and ROBERT ALBERT (*J. pr. Chem.*, 1904, [ii], 70, 509—515).—Cassell brown, sold as an artist's colour, contains 90 per cent. of humus substances, from which humic acid, containing only 0.87 per cent. of ash, is obtained by extraction with lithium carbonate and water and addition of hydrochloric acid to the filtrate. Humic acid so obtained gives C=60.03, H=4.40, N=1.09 per cent.; when treated with concentrated nitric acid, it forms a reddish-brown *nitro*-derivative, which has the composition C=55.52, H=4.51, N=3.80, S=0.92, ash=0.82 per cent., is easily soluble in methyl or ethyl alcohol, glacial acetic acid, or acetone, and, when heated with bromine or glacial acetic acid in a sealed tube at 100°, yields a *bromo*-derivative containing 41—43 per cent. of bromine.

G. Y.

Aminoethyl Ether. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 984—994. Compare Knorr, *Abstr.*, 1904, i, 854).—The author has shown (*Abstr.*, 1901, i, 16) that in two carbon compounds the substitution of the OH group by NH₂ leads to an abnormal rise in boiling point when an amino-alcohol is the product of the reaction, and has ascribed this to the mutual influence of the OH and NH₂ groups. He now points out that the substitution of an OEt group by NH₂ in such cases with the formation of an amino-ether gives rise to a normal increase in boiling point, affording evidence of the validity of his explanation. Thus the difference between the boiling points of ethyl ether and ethylamine is 16°, and that between those of the diethyl ether of glycol and aminoethyl ether is 14° or 15°. Further evidence of the mutual influence of the OH and NH₂ groups in the amino-alcohols is afforded by a comparison of their densities in the liquid state with those of the corresponding alcohols and amines.

The substitution of OH by OEt in compounds of the type XCH₂·CH₂·OH leads to a fall in the boiling point, and the amount of this depends on both the mass and the nature of the group X. These statements are illustrated by examples in the original.

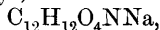
T. A. H.

Synthesis of Serin and Cystin. EMIL ERLÉNMEYER, jun., and F. STROOP (*Annalen*, 1904, 337, 236—263. Compare *Abstr.*, 1903, i, 29, 791).—The synthesis of serin (α -amino- β -hydroxypropionic acid) has been achieved by a method differing materially from that of Fischer and Leuchs (*Abstr.*, 1903, i, 12).

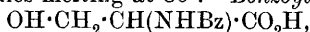
Ethyl hippurate condenses with ethyl formate forming the oxy-

methylene compound, $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{NHBz})\cdot\text{CO}_2\text{Et}$, which, on reduction, gives the ester of benzoylserin, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{Et}$; the latter can be hydrolysed either to benzoylserin or to serin.

Ethyl hippurate is best prepared by passing hydrogen chloride into a boiling solution of hippuric acid in alcohol and crystallising the product from benzene or ether. When treated with sodium ethoxide, the ester yields a *sodium* derivative, $\text{ONa}\cdot\text{CPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, as a white, crystalline precipitate. *Ethyl formylhippurate* was prepared by adding ethyl formate to a solution of sodium ethoxide, when the sodium derivative separates; unless both the alcohol and the sodium are quite pure, decomposition takes place with the evolution of carbon monoxide. Ethyl hippurate is now added, when the mixture sets to a crystalline mass and is kept for ten days, when the *sodium* derivative,

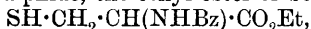


is collected; the *ester* is difficult to obtain from the sodium derivative in a solid state, but when pure crystallises in needles melting at 128° . The *ethyl* ester of *benzoylserin* is prepared by reducing the ethyl formylhippurate with aluminium amalgam in moist ether, and crystallises from benzene in needles melting at 80° . *Benzoylserin*,



is prepared by hydrolysis of the ester by alcoholic sodium hydroxide, and forms crystals melting at 159° . The ester of benzoylserin can be converted into serin by prolonged boiling with sulphuric acid (1 in 15), the use of sulphuric acid of any other strength either not effecting the hydrolysis or causing decomposition; the serin was characterised by conversion into its copper salt, and by measurement of the crystals.

Baumann's formula for cystein, $\text{SH}\cdot\text{CMe}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, which was long accepted as correct, represents this substance as a derivative of thiopyruvic acid. There is no strong evidence, however, in favour of this formula: the known facts rather support one of the expressions $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ or $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{SH})\cdot\text{CO}_2\text{H}$; since the former represents it as a thioserin, it is the more probable. The work of Neuberg (Abstr., 1902, i, 743) and Friedmann (Abstr., 1902, i, 731; 1903, i, 75, 301) has shown this view to be correct. The synthesis of serin, therefore, rendered possible a synthesis of cystine, and it was found that the oxygen of the hydroxy-group in the ethyl ester of benzoylserin could be replaced by sulphur by the action of phosphorus pentasulphide, the ethyl ester of benzoylcystein,



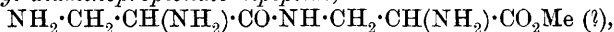
being produced. The ester is molten with twice the theoretical quantity of phosphorus pentasulphide, being heated finally for 8 hours at 120° ; the product is extracted with alcohol and recrystallised from ether; it forms colourless needles melting at 158° . On boiling the ester with hydrochloric acid, it is hydrolysed to cystein, which was recognised by means of the additive compound with mercuric chloride. Cystein is very readily oxidised to cystin, the process being best carried out by drawing air through the warmed solution in ammonia. The cystin thus obtained was identical in all respects with the natural cystin prepared from urine with the exception that it was inactive towards polarised light.

K. J. P. O.

Polypeptides of the Diamino-acids. EMIL FISCHER and UMETARO SUZUKI (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1333—1341. Compare Abstr., 1903, i, 645, 799, 800; 1904, i, 771; this vol., i, 30).—The diamino-acids, so important biologically, are converted, on heating their methyl esters, into dipeptide and diketopiperazine derivatives.

Methyl diaminopropionate hydrochloride, $C_4H_{10}O_2N_2 \cdot 2HCl$, conveniently prepared by the action of dry methyl alcohol and hydrogen chloride on the hydrochloride of diaminopropionic acid, melts and decomposes at 166° (corr.); the free ester is obtained from this by the action of sodium and methyl alcohol as a colourless, strongly alkaline syrup.

Methyl diaminopropionate dipeptide,



is prepared by heating the foregoing ester at 100° for an hour, and purified by conversion into the picrate or hydrochloride. The *picrate* forms yellow crystals sparingly soluble in water, which, on heating, darken at 170 — 180° and melt and decompose between 200° and 210° ; the *hydrochloride* is an almost colourless, dense powder sintering at 90° and decomposing at 135° .

Methyl lysine hydrochloride, prepared by the action of methyl alcohol and hydrogen chloride on *r*-lysine hydrochloride, crystallises in colourless, oblique prisms, melting and decomposing at 218° . *Lysine anhydride* is obtained on heating methyl lysine at 100° , as a slightly brown, limpid mass; the *picrate*, $C_{12}H_{24}O_2N_4 \cdot 2C_6H_3O_7N_3$, crystallises from water in small, yellow prisms or plates which, when heated, darken at 210° and melt and decompose at 230° (corr.); the *hydrochloride* forms microscopic, colourless needles melting and decomposing at 270° (corr.).

Histidine anhydride, $C_{12}H_{14}O_2N_6$, prepared from the methyl histidine hydrochloride described by Pauly (Abstr., 1904, i, 1068), crystallises in colourless, glistening prisms, darkening about 260° and melting to a brown liquid at about 340° .

Methyl arginine hydrochloride, prepared from the double salt of arginine and copper nitrate, crystallises in long, colourless needles or prisms melting and decomposing at 195° (corr.). E. F. A.

Action of Potassium Thiocyanate on Metallic Oxides at High Temperatures. JAR. MILBAUER (*Zeit. anorg. Chem.*, 1904, 42, 433—449).—Potassium thiocyanate melts at 171 — 172° , becomes brown at 300° , and assumes a blue tint at 405° . It was heated with various metallic oxides in vessels of porcelain or of glass, and at temperatures ranging from 200° to 1200° . At 300° , lead monoxide reacts with potassium thiocyanate according to the equation $PbO + KCNS = PbS + K_2CO_3$. The action of zinc oxide and of cadmium oxide is similar. The action with stannic oxide proceeds in two stages, namely: (1) $2KSCN + SnO_2 = SnS + K_2S + 2CO + N_2$ and (2) $KCNS + K_2S + SnS = K_2SnS_3 + KCN$, the latter action proceeding at a temperature higher than that at which the first action takes place. When manganous oxide was used, manganese sulphide was generally produced; in one case, manganese potassium sulphide was isolated. With cupric oxide, cuprous sulphide was produced, whilst

the double sulphide $K_2Cu_8S_6$ was formed at more elevated temperatures, thus: $2CuO + 2KSCN = Cu_2S + K_2S + 2CO + N_2$ and $4Cu_2S + K_2S + KSCN = K_2Cu_8S_6 + KCN$. With molybdenum oxide, the sulphides MoS_2 and MoS_3 were isolated. Bismuth oxide yielded bismuth sulphide, mixed with the double sulphide $Bi_2K_2S_4$ when higher temperatures were employed. Chromium oxide yielded the compound $K_2Cr_2S_4$, which forms glistening, metallic, greenish-grey crystals, insoluble in warm hydrochloric acid, and which at a red heat decompose to form sulphur dioxide and chromium oxide. Its formation is represented by the equations: (1) $Cr_2O_3 + 3KSCN = Cr_2S_3 + 3KCNO$, (2) $2KCNO + KSCN = K_2S + KCN + 2CO + N_2$, (3) $Cr_2S_3 + K_2S = K_2Cr_2S_4$. With ferric oxide at 400° , the sulphide $K_2Fe_2S_4$ was produced. Cobalt oxide formed the sulphide $K_2Co_{11}S_{10}$, the action of nickel oxide being analogous.

From the mixture of oxides obtained by heating uranyl acetate, the sulphide UO_2S was isolated. A. McK.

Compound Thiocyanates of Palladium. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 386—393).—Palladium resembles platinum in forming double thiocyanates of the form $Pd(SCN)_4X_2$, but the corresponding compounds derived from quadrivalent palladium either do not exist or are unstable, and when attempts are made to prepare them the bivalent palladium compounds are always obtained.

Palladous thiocyanate, $Pd(SCN)_2$, forms a reddish, flocculent precipitate, which dissolves readily in potassium thiocyanate solution yielding *potassium palladothiocyanate*, $Pd(SCN)_4K_2$, separating from water in ruby-red, acicular crystals. This double salt, which is best obtained from potassium palladochloride (1 mol.) and potassium thiocyanate (4 mols.), is a true complex salt, as is seen from a comparison of the electrical conductivity of its solutions with that of the corresponding platinum compound.

Silver palladothiocyanate, $Pd(SCN)_4Ag_2$, is an insoluble, amorphous, red salt, whilst the *barium* salt is crystalline and very readily soluble in water. The free acid is unstable and could not be prepared.

T. H. P.

5-Methylbarbituric Acid. EMIL FISCHER (*Annalen*, 1904, 336, 345. Compare this vol., i, 37).—5-Methylbarbituric acid has been previously described as *isosuccinic-ureide* by Franchimont and Klobbie (Abstr., 1888, 1181).

G. Y.

Attempts to Synthesise Nitroacetonitrile. WILHELM STEINKOPF (*Ber.*, 1904, 37, 4623—4627. Compare Ratz, Abstr., 1904, i, 857).—An attempt was made to prepare ethyl nitroacetate by distilling potassium ethyl malonate, $CO_2Et \cdot CHCl \cdot CO_2K$, with aqueous potassium nitrite, but the principal product was simply ethyl chloroacetate formed by the decomposition of the malonate by water. Nitroacetamide (Ratz, *loc. cit.*) was obtained by heating Bouveault and Wahl's nitroacetic acid (Abstr., 1904, i, 795) in the form of its ammonium salt with concentrated alcoholic ammonia for 2 hours at 100° ; the immediate product is ammonium nitroacetamide, $C_2H_7O_3N_3$,

which crystallises in long, yellow needles, melts at 152° , and on treatment with dilute sulphuric acid liberates nitroacetamide, melting at 101 – 102° ; Ratz gives the melting points for these two substances as 148° and 98° , but the author, by using Ratz's method, obtained products identical in melting point with his own. W. A. D.

Monomethyl-tin Derivatives. III. PAUL PFEIFFER [with IDA HELLER] (*Ber.*, 1904, 37, 4618–4620. Compare Abstr., 1903, i, 470, 802, and Pope and Peachey, *ibid.*, 741).—Methylstanniodoform (tinmethyl iodide), SnMeI_3 , is readily obtained by heating stannous iodide with methyl iodide for 4 hours at 160° ; the best method of preparing it, however, consists in boiling an ethereal solution of magnesium methyl iodide with stannic iodide. W. A. D.

Preparation of Cyanides from Ferrocyanides. GROSSMAN'S CYANIDE PATENTS SYNDICATE (D.R.-P. 156397. Compare Abstr., 1904, 562, 860).—The iron alkali ferrocyanide ("Everitt's salt"), obtained in the preparation of hydrogen cyanide from ferrocyanides, may be oxidised to Prussian blue and then decomposed by an alkali in order to recover the ferrocyanide. The oxidation, however, proceeds with difficulty with the usual oxidising agents. When air is blown into the solution, oxidation takes place rapidly. The reaction is best carried out by adding a ferrous salt and passing a current of air through the boiling solution. The oxidation takes place quantitatively, and the ferrous salt is continually regenerated: $3\text{Na}_2\text{Fe}_2\text{Cy}_6 + 2\text{Fe}_2\text{Cl}_6 = \text{Fe}_7\text{Cy}_{18} + 3\text{FeCl}_2 + 6\text{NaCl}$. C. H. D.

Preparation of Sodium Ferrocyanide from Calcium Ferrocyanide. ADMINISTRATION DER MINEN VON BUCHSWEILER (D.R.-P. 155806).—In the preparation of potassium ferrocyanide from a solution of calcium ferrocyanide, one-half of the calcium may be replaced by the addition of potassium chloride, the sparingly soluble double salt, $\text{K}_2\text{CaFe}(\text{CN})_6$, being precipitated. Sodium does not form a similar salt, and the addition of sodium hydroxide or carbonate has therefore been necessary to remove the calcium. It is, however, possible to separate the sodium ferrocyanide and calcium chloride, formed according to the equation $\text{Ca}_2\text{Fe}(\text{CN})_6 + 4\text{NaCl} = \text{Na}_4\text{Fe}(\text{CN})_6 + 2\text{CaCl}_2$, by crystallisation, the calcium chloride remaining in solution. The sodium ferrocyanide is not decomposed during evaporation. C. H. D.

New Additive Compounds of Tetrahydrobenzene. LÉON BRUNEL (*Compt. rend.*, 1904, 139, 1029–1031. Compare Abstr., 1903, i, 157, 338).—*o*-Iodocyclohexyl acetate, $\text{C}_6\text{H}_{10}\text{I}\cdot\text{OAc}$, obtained by the action of mercuric oxide, iodine, and acetic anhydride on cyclohexene in ethereal solution, is a yellow oil with an aromatic odour, soluble in the ordinary organic solvents, has a sp. gr. 1.61 at 0° , and decomposes when distilled under reduced pressure. *o*-Iodocyclohexyl propionate, $\text{C}_6\text{H}_{10}\text{I}\cdot\text{CO}_2\text{Et}$, similarly prepared, is a yellow oil having a sp. gr. 1.64 at 0° .

The mercuric oxide and acid anhydride in the above reactions can be replaced by the mercuric salt of the corresponding acid.

M. A. W.

Preparation of Benzene free from Sulphur. CARL SCHWALBE (*Zeit. Farb. Text. Ind.*, 1904, 3, 461—464).—The carbon disulphide present in commercially purified benzene is best removed by passing moist gaseous ammonia through the hydrocarbon, and subsequently washing it with dilute sulphuric acid. The thiophen is most completely eliminated by passing nitrous fumes, from sodium nitrite and sulphuric acid, through the liquid, and subsequently shaking it two or three times with concentrated sulphuric acid. Shaking the oil with sulphuric acid containing nitrous fumes is not so advantageous.

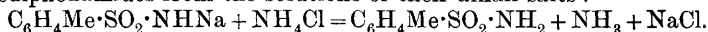
W. A. D.

***o*-Chloro-*m*-nitrotoluene-*ω*-sulphonic Acid.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 154493).—Sodium hydrogen sulphite converts *o*-chlorobenzyl chloride into *o*-chlorotoluene-*ω*-sulphonic acid, the sodium salt of which crystallises in glistening leaflets. On nitrating in sulphuric acid solution, *o*-chloro-*m*-nitrotoluene-*ω*-sulphonic acid is obtained. The sodium salt crystallises from hot water in yellow needles. The chlorine atom is readily displaced by ammonia or amines.

Permanganates oxidise the acid to 2-chloro-5-nitrobenzoic acid.

C. H. D.

Separation of Toluene-*o*- and -*p*-sulphonamides. RUDOLF BARGE & LÉON GIVANDAN (D.R.-P. 154655).—Ammonium salts may be employed in place of acids or acid salts to precipitate toluene-*o*- and -*p*-sulphonamides from the solutions of their alkali salts:



A better fractional separation is obtained than when acids are used. The ammonium chloride solution obtained in the preparation of the sulphonamides from the sulphonic chlorides may be employed, and the ammonia produced may be recovered.

C. H. D.

Dibromoanthracene Tetrabromide. FELIX KAUFLE and M. IMHOFF (*Ber.*, 1904, 37, 4706—4709).—The difference in melting point between the bromoanthraquinone, prepared by Graebe and Liebermann from tribromoanthracene, and the β -bromoanthraquinone, prepared from β -aminoanthraquinone (Abstr., 1904, i, 256), is due to the presence of 2:6:9:10-tetrabromoanthracene in the former product.

Tetrabromoanthracene, prepared by heating dibromoanthracene tetrabromide at 200° until the evolution of bromine and hydrogen bromide ceased, melts at 298—300°, and, when oxidised in glacial acetic acid solution by chromic acid, forms *dibromoanthraquinone*, which melts at 289—290°. During the preparation of tetrabromoanthracene, tribromoanthracene was also formed. The bromoanthraquinone, prepared by oxidising the latter, melted at 201—202° and was identical with the β -compound, obtained from β -aminoanthraquinone by the diazo-reaction.

2:6-Diaminoanthraquinone was converted into 2:6-anthraquinone-

tetrazonium perbromide, which, when heated at 170° , formed 2:6-dibromoanthraquinone, identical with the product obtained from dibromoanthracene tetrabromide. The bromine atoms in the tetrabromoanthracene described are accordingly in the 2:6:9:10-position.

A. McK.

Separation of the Three Dimethylantracenes obtained in the Action of Methylene Chloride and Aluminium Chloride on Toluene. JAMES LAVAUX (*Compt. rend.*, 1905, 140, 44—45. Compare this vol., i, 43).—Experimental details connected with the working up of the products of the reaction are communicated, for which the original must be consulted. The three dimethylantracenes, which are simply referred to as *A*, *B*, and *C*, melt respectively at 240° , 244.5° , and 86° .

H. M. D.

Ullmann and Borsum's "Hexaphenylethane"; Tervalency of Carbon. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1904, 37, 4709—4715).—The constitution of the hydrocarbon described by Ullmann and Borsum as hexaphenylethane (*Abstr.*, 1902, i, 755) is discussed. If this hydrocarbon were hexaphenylethane, it should undergo oxidation to triphenylcarbinol, which it does not do. Further, its formation takes place under abnormal conditions where the presence of condensing agents is necessary. The author supposes that the hydrocarbon in question is not hexaphenylethane, but diphenylmethyl-tetraphenylmethane, formed in accordance with the equation $\text{CPh}_3 \cdot \text{OH} + \text{C}_6\text{H}_5 \cdot \text{CHPh}_2 = \text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2 + \text{H}_2\text{O}$. Evidence for this view is afforded by the action of bromine on the hydrocarbon, which is proved to contain one hydrogen atom, combined like the hydrogen atom of the (CH) group in triphenylmethane.

This result makes it more probable than before that Gomberg's triphenylmethyl is in reality hexaphenylethane, especially since Gomberg himself has shown that his hydrocarbon has a molecular weight double that corresponding with triphenylmethyl.

Bromine was gradually added in direct sunlight to a solution of Ullmann and Borsum's hydrocarbon in carbon disulphide. Only one molecular proportion of bromine interacted, and the *monobromide* was produced in almost quantitative yield as faintly yellowish-red crystals melting at 240 — 242° . This compound resembles triphenylbromomethane and reacts readily with water, alcohol, and acetic acid respectively, its action with water being represented as follows: $\text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2\text{Br} + \text{H}_2\text{O} = \text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OH} + \text{HBr}$. The latter reaction proceeds quantitatively when the solution of the bromide in pyridine is decomposed by hot water, the *carbinol*, $\text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OH}$, separating as a white powder, which crystallises from a mixture of benzene and light petroleum in glistening balls and melts at 220 — 220.5° . It forms a brownish-red solution with concentrated sulphuric acid, differing in this respect from the original hydrocarbon.

A. McK.

Nitrophenylcyanamides. PAUL PIERRON (*Bull. Soc. chim.*, 1905, [iii], 33, 69—74).—*o*-Nitrophenylcyanamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CN}$, ob-

tained by heating in closed vessels cyanogen bromide dissolved in water with *o*-nitroaniline in alcohol, crystallises in bright yellow needles, melts at 146° , is readily soluble in alcohol, and fairly so in ether. The *benzoyl* derivative crystallises in almost colourless needles from alcohol and melts at 105° .

m-Nitrophenylcyanamide, prepared by boiling together cyanogen bromide and *m*-nitroaniline dissolved in a mixture of water and alcohol, crystallises in short, pale yellow needles, melts at 130° , and is soluble in alcohol, less so in ether or benzene. The *benzoyl* derivative crystallises in pale yellow lamellæ, melts at 109° , and is soluble in alcohol or ether and less so in benzene.

p-Nitrophenylcyanamide, similarly prepared, crystallises in bright yellow needles, melts at 180° , and probably polymerises at the same time. It is very soluble in alcohol, less so in ether, and slightly so in benzene. The *benzoyl* derivative crystallises in almost colourless lamellæ, melts at 131° , and is less soluble in alcohol than its isomerides.

p-Nitrophenylcarbamide, obtained by heating the cyanamide, dissolved in alcohol, with hydrochloric acid, forms short prisms when crystallised by cooling a concentrated solution in alcohol and separates in needles from alcohol at 40° ; it melts at 238° , is soluble in alcohol, and slightly so in benzene or ether. On reduction with tin and hydrochloric acid, it yields *p*-aminophenylcarbamide (m. p. 129°), and when heated with hydrochloric acid for from 10 to 12 hours furnishes *p*-nitroaniline.

T. A. H.

Preparation of *o*-Chlorophenol. WILHELM LOSSEN (D.R.-P. 155631. Compare Hazard-Flamand, Abstr., 1903, i, 622).—Phenol may be directly chlorinated at a low temperature in an indifferent solvent, such as carbon tetrachloride, chloroform, or a liquid hydrocarbon. Solutions of phenol and chlorine may be mixed or a current of gaseous chlorine may be employed. The pure *o*-chlorophenol is isolated from the product in the usual manner.

C. H. D.

Picrolonates derived from Substances[Amines] of Physiological Importance. J. OTORI (*Zeit. physiol. Chem.*, 1904, 43, 305—315. Compare Knorr and Mathes, Abstr., 1899, i, 462; Steudel, *ibid.*, 1903, i, 431).—Pentamethylenediamine picrolonate, $C_5H_{10}(NH_2)_2 \cdot 2C_{10}H_8O_5N_4$, obtained by mixing alcoholic solutions of the acid and of the hydrochloride of the base, crystallises in slender, orange-yellow needles or plates, begins to turn brown at 220° , and decomposes sharply at 250° . One part dissolves in 7575 of water at 16° or 357 at 100° , and in 5952 parts of cold or 475 of boiling alcohol. When prepared from the carbonate of the base, it decomposes at the same temperature, 250° , but differs as regards its solubility.

Tetramethylenediamine picrolonate crystallises in yellow needles, decomposes at 263° when slowly heated, and is very sparingly soluble. One part dissolves in 13,157 parts of cold or in 653 parts of hot water; also in 17,857 parts of cold or 954 of hot alcohol.

Picrolonate of	No. of molecules of acid combined with one of base.	Decomposes at	One part dissolves in			
			Water.		Alcohol.	
			Cold.	Boiling.	Cold.	Boiling.
Methylamine	2	244°	1073	369	4717	133
Dimethylamine	1	222	764	33	853	38
Trimethylamine	1	250—252	1121	166	794	223
Ethylamine	1	244	3846	93	1700	76
Diethylamine from hydrochloride	1	260	3788	402	2941	213
Diethylamine from carbonate	1	260	1984	276	2193	297
Triethylamine	1	160	536	63	494	87
Betaine	1	200	—	—	—	—
		(or from carbonate at 192°)				
Choline	1 + 1 H ₂ O	melts at 158° decomposes at 241—245°	—	—	—	—
Neurine	1	233	—	—	—	—
Lysine	1	246—252	—	readily	soluble	—

J. J. S.

Alkyl Ethers of *p*-Allylphenol. ALBERT VERLEY (D.R.-P. 154654).—*p*-Bromoanisole and its homologues react with magnesium in ethereal solution to form compounds having the constitution $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{MgBr}$, which then react with allyl haloids forming *p*-allylanisole and its homologues.

p-Allylanisole, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_3\text{H}_5$, boils at 108—114° under 25 mm. pressure, and is converted into the propenyl compound, anethole, by boiling with alcoholic potassium hydroxide. *p*-Allylphenetole boils at 113—114° under 20 mm. and at 224° under 750 mm. pressure; *p*-propenylphenetole boils at 241° under 750 mm. pressure and melts at 61°.

C. H. D.

[4-Phenoxy-2-aminobenzenesulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156156).—On heating a solution of sodium 4-chloro-3-nitrobenzenesulphonate and sodium phenoxide, sodium 4-phenoxy-2-nitrobenzenesulphonate, $\text{OPh} \cdot \text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{SO}_3\text{Na}$, is produced. It yields on reduction 4-phenoxy-2-aminobenzenesulphonic acid, crystallising from water in glistening, white leaflets. The diazo-compound is stable and dissolves sparingly in water; it yields a red azo-dye with β -naphthol.

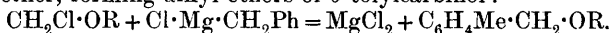
C. H. D.

Aminoacetylcatechol. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 155632).—Aminoacetylcatechol may be prepared by

the method employed for the preparation of its alkyl derivatives (Abstr., 1904, i, 873), ammonia being used in place of alkylamines. Chloroacetylcatechol at first combines with ammonia to form the sparingly soluble ammonium salt, which then passes spontaneously into the amino-compound, which is isolated in the form of its hydrochloride.

Aminoacetylcatechol, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot NH_2$, forms a crystalline powder, dissolving sparingly in water, alcohol, or ether. The *hydrochloride* crystallises from alcohol in colourless leaflets, decomposing at 260° , and dissolves readily in water. C. H. D.

[Alkyl Ethers of *o*-Tolylcarbinol.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 154658).—Chloromethyl alkyl ethers react with the double compounds of magnesium benzyl haloids and benzyl ether, forming alkyl ethers of *o*-tolylcarbinol:



o-Tolylcarbinyll methyl ether, $C_6H_4Me \cdot CH_2 \cdot OMe$, is a colourless oil with aromatic odour and boils at 187 — 188° . The *ethyl ether* boils at 202 — 203° ; the *amyl ether* boils at 124° under 15 mm. pressure.

C. H. D.

[Colourless Salts of Triphenylcarbinol and Diphenylcarbinol.] RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1904, 37, 4647).—An historical correction (compare *Ber.*, 1904, 37, 3058). W. A. D.

Action of Light on Cholesterol. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1904, 43, 316—319).—When cholesterol is exposed to bright sunlight for some time, it turns yellow, its melting point is considerably lowered, and it ceases to give the characteristic reactions with acetic anhydride and sulphuric acid or with vanillin and hydrochloric acid. All these changes are due to the formation of a small amount of brownish-yellow substance, which remains in the mother liquor when the cholesterol is crystallised from alcohol. Cholesterol is not affected when sealed in a glass tube containing carbon dioxide and then exposed to light. J. J. S.

Cholesterol. IV. ADOLF WINDAUS (*Ber.*, 1904, 37, 4753—4756. Compare Abstr., 1904, i, 49, 667 and 1010. Compare Diels and Abderhalden, *ibid.*, 880).—Bromocholestanonic acid (Abstr., 1904, i, 667), when heated with glacial acetic acid containing hydrochloric acid, is converted into the lactone, $C_{27}H_{40}O_5$, of a hydroxycholestanonic acid; the lactone crystallises from alcohol in long needles, melts after sintering at 192 — 193° , and behaves on titration with cold aqueous sodium hydroxide as a monobasic acid, but with the hot alkali as a dibasic acid. On heating the lactone-acid with 10 per cent. aqueous potassium hydroxide for two hours, it is transformed into a *hydroxy-ketodicarboxylic acid*, $C_{27}H_{42}O_6$, which crystallises from diluted acetic acid, melts at 174 — 175° , and, as it does not give a lactone, is isomeric with the acid corresponding to the lactone just described. This acid

can be readily obtained by heating bromocholestanonic acid directly with aqueous potassium hydroxide; as it is very resistant to chromic acid, it probably contains a tertiary hydroxyl radicle. W. A. D.

Dehydration of α -isoDypnopinacolin. I. ÉGIDE TERLINCK (*Bull. Acad. Roy. Belg.*, 1904, 1049—1086. Compare Delacre and Gesché, *Abstr.*, 1904, i, 32).—The first part of the paper gives detailed descriptions of methods for the preparation and isolation of α -isodypnopinacolin, homodypnopinacolin, and the hydrocarbon, $C_{25}H_{22}$, from dypnone or acetophenone (compare Delacre, *Abstr.*, 1896, i, 591; 1900, i, 603, and Gesché, 1900, i, 604; 1903, i, 484).

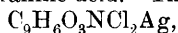
By the dehydration of α -isodypnopinacolin, the α - and β -isodypnopinacolenes, $C_{32}H_{24}$, are formed (compare Delacre, *Abstr.*, 1896, i, 591). The dehydration may be brought about by mixtures of acetic acid with sulphuric, hydrochloric, or hydrobromic acid, or by acetyl chloride. The relative amounts of the two isomerides formed varies with the nature of the dehydrating agent employed, a "strong" acid favouring the production of β -isodypnopinacolene (m. p. 171°) and a feeble one the formation of the isomeride. No evidence of the conversion of one isomeride into the other by the action of these dehydrating agents was obtained. α -isoDypnopinacolene crystallises from acetic acid or alcohol in lamellæ, melts at 175.5° , and distils under atmospheric pressure with the formation of a small quantity of the β isomeride. When heated with potassium hydroxide at 220° , it is converted into a *product*, $C_{32}H_{20}O$, which crystallises from chloroform on addition of ether in needles or parallelepipeds and melts at 173° . With sulphuric acid, there is formed a *derivative* (sulphonic?) which crystallises in white spangles and is soluble in water, from which it is reprecipitated by ammonium chloride. Nitric acid, acting on α -isodypnopinacolene dissolved in acetic acid, converts it into a *nitro-derivative*, $C_{32}H_{23}O_2N$; this crystallises from dilute acetic acid or nitrobenzene in hard, yellow crystals and melts at 272° . On reduction, α -isodypnopinacolene does not yield definite products, but on oxidation by chromic acid in presence of acetic acid a small quantity of benzoic acid is formed.

When the hydrocarbon is dissolved in carbon disulphide and treated with a molecular proportion of bromine, a *bromo-derivative*, $C_{32}H_{25}Br$, is produced, which crystallises in pale yellow needles, melts at 199 — 200° , and on reduction with sodium amalgam in presence of alkalis furnishes a series of crystalline products. When chloroform is employed as the solvent, an isomeric *bromo-derivative* is obtained; this crystallises in tablets, melts at 192° , and furnishes a crystalline reduction product with sodium amalgam. When the bromination is carried out in presence of acetic acid, a crystalline product of indefinite composition is formed. A *dibromo-derivative* forming large, cubical crystals is obtained when bromine (2 mols.) is added to α -isodypnopinacolene dissolved in carbon disulphide. When the hydrocarbon is mixed with reduced iron and excess of bromine added, a vigorous reaction ensues and the principal product is the *compound* $C_{32}H_{14}Br_{10}$; this crystallises from chloroform on addition of ether in straw-coloured tablets, retains chloroform tenaciously, develops a violet colour on exposure to sunlight, evolves hydrogen bromide and becomes resinous

when heated, and when warmed with potassium hydroxide in alcohol furnishes a bright red solution. T. A. H.

Constitution of Anthranil. GUSTAV HELLER (*J. pr. Chem.*, 1904, [ii], 70, 516—520. Compare Abstr., 1902, i, 779; 1903, i, 827; 1904, i, 160).—A reply to Bamberger (Abstr., 1904, i, 422). G. Y.

Chloralamino-compounds. II. SIMON GÄRTNER (*Annalen*, 1904, 336, 229—246. Compare Abstr., 1904, i, 788).—Trichloroethylidene-anthranilic acid and potassium cyanide react in aqueous solution, at the ordinary temperature, to form a product which, when boiled with water, yields dichloroacetylanthranilic acid (Jackson, Abstr., 1881, 735); this is also formed by the action of dichloroacetic chloride on anthranilic acid; it crystallises in colourless needles or large, colourless plates, melts at 176—177°, is hydrolysed by aqueous sodium hydroxide, or, less easily, by dilute sulphuric acid, to anthranilic, dichloroacetic, and glycollic acids, and is reduced by sodium amalgam in aqueous solution to anthranilic acid. The *silver* salt,



crystallises in rosettes of needles; the *ethyl* ester, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{NCl}_2$, crystallises in rhombic plates, melts at 58—60°, and boils at 180—190° under 13 mm. pressure. The *silver*, *barium*, and *calcium* salts of anthranilic acid are described.

When boiled with acetic anhydride, dichloroacetylanthranilic acid forms the *lactone* of its tautomeric form, $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N}=\text{C}\cdot\text{CHCl}_2 \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, which

crystallises in long, colourless prisms, melts at 175°, is easily soluble in acetone or chloroform, and is hydrolysed, when boiled with water, to the dichloro-acid. When boiled with 20 per cent. ammonia in a reflux apparatus, the lactone forms dichloroacetylanthranilimine (4-keto-

2-dichloromethyldihydroquinazoline), $\text{C}_6\text{H}_4\text{<}\begin{smallmatrix} \text{N}=\text{C}\cdot\text{CHCl}_2 \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$, which

tallises in thick rhombohedra, melts at 210°, sublimes without decomposition, and, when dissolved in warm aqueous sodium hydroxide, is converted into an *amino*-acid. The action of phenylhydrazine on the lactone leads to the formation of two substances: a *chloro*-compound, $\text{C}_{21}\text{H}_{18}\text{ON}_5\text{Cl}$, which crystallises in red plates and melts and decomposes at 248°, and a *derivative*, $\text{C}_{21}\text{H}_{17}\text{ON}_5$, which crystallises in glistening needles and melts and partly decomposes at 232°. G. Y.

ω -Sulphomethylantranilic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 155628).—Formaldehyde and anthranilic acid combine in aqueous suspension or ethereal solution to form a condensation product, separating in yellowish-white crystals melting at about 145—150°, insoluble in water or dilute acids, readily soluble in acetone. The compound becomes luminous on rubbing. Sodium sulphite converts it into *ω -sulphomethylantranilic acid* (sulphite compound of methyleneanthranilic acid), which reacts with metallic cyanides to form *ω -cyanomethylantranilic acid* (compare Abstr., 1903, i, 336). C. H. D.

α -Amino-acids. EMIL ERLENMEYER, jun. (*Annalen*, 1904, 337, 205—221).—An account is given of the various methods of preparing α -amino-acids, including some recent and new methods devised by the author, in which aldehydes are condensed with glycine and analogous substances. The synthesis of α -amino- β -hydroxy-acids by similar methods is also described. The paper concludes with a discussion of the state of our knowledge of the property exhibited by the methylene group of inducing condensation with various substances.

K. J. P. O.

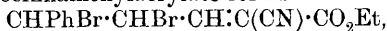
Synthesis of some α -Amino- β -hydroxy-acids. EMIL ERLENMEYER, jun., and F. BADE (*Annalen*, 1904, 337, 222—235. Compare preceding abstract).—The number of aldehydes which are able to condense with glycine forming α -amino- β -hydroxy-acids is very limited. Neither vanillin nor salicylaldehyde will condense in this manner. *o*-Methoxybenzaldehyde (2 mols.), however, condenses with glycine (1 mol.) when they are shaken together in the presence of a 50 per cent. solution of sodium hydroxide to which alcohol has been added; the product solidifies, a mixture of two substances being formed which are separated by crystallisation from alcohol. The less soluble is the sodium salt, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CO}_2\text{Na}, \frac{1}{2}\text{EtOH}$, which forms rhombs. The free acid could not be obtained, but its *acetyl* derivative, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OAc})\cdot\text{C}(\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CO}_2\text{H}, \text{H}_2\text{O}$, is obtained, together with a neutral yellow substance, when the sodium salt is heated with acetic anhydride at 100° ; it forms crystals, becoming yellow at 210° and decomposing at 216° . When a solution of the sodium salt is treated with dilute acetic acid, *o*-methoxyphenylserine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}, \text{H}_2\text{O}$, is obtained, *o*-methoxybenzaldehyde being eliminated; this acid crystallises in leaflets very soluble in water, and melting and decomposing at 179° ; the *hydrochloride* is a crystalline powder, and the *copper* salt a greyish-blue, insoluble powder. When heated with acetic anhydride, the amino-acid is converted into the *oxazole*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, which

crystallises in yellow leaflets melting at 156° ; it is identical with the yellow substance formed when the sodium salt is heated with acetic anhydride. On boiling the oxazole with sodium hydroxide, it is converted into the *acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{NHAc})\cdot\text{CO}_2\text{H}$, which crystallises in small needles melting and decomposing at 214° .

The soluble substance formed in the condensation is best prepared by using 3 mols. of the *o*-methoxybenzaldehyde, and is a compound formed by condensation of 3 mols. of the aldehyde with glycine, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$; it crystallises in needles melting at 134° , and in alcohol gives an alkaline reaction. When heated with acetic anhydride, it yields an *acetyl* derivative melting at 170° . On warming with hydrochloric acid at 100° , the free *base*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is obtained, crystallising in needles melting at 136° ; the *platinichloride* crystallises from alcohol and melts at 197° . When heated, the base decomposes into *o*-methoxybenzaldehyde and *o*-methoxybenzylamine (*o*-anisamine), which is an oil; the *hydrochloride* crystallises in long needles melting

at 149°, and the *platinichloride*, $(C_8H_{11}ON)_2 \cdot H_2PtCl_6 \cdot 2\frac{1}{2}H_2O$, in dark yellow leaflets melting and decomposing at 189°. K. J. P. O.

Unsaturated Compounds. II. F. WILLY HINRICHSSEN (*Annalen*, 1904, **336**, 323—344. Compare Abstr., 1902, i, 129; 1904, i, 1012).—[With OSCAR LOHSE.]—When acted on by bromine in chloroform solution, ethyl α -cyanocinnamenylacrylate forms a *dibromide*,



which melts at 98°, and is oxidised by chromic acid in glacial acetic acid solution to the dibromide of cinnamic acid. The *dibromide* of cyanocinnamenylacrylic acid melts at 187° and yields the ethyl ester melting at 98°.

Cinnamylidenemalononitrile, $CHPh:CH \cdot CH:C(CN)_2$, obtained by the condensation of cinnamaldehyde with methylene dicyanide in presence of sodium ethoxide, crystallises in slender, yellow needles, melts at 128°, and forms a white, crystalline dibromide,



which melts at 130°, and, on oxidation, yields benzoic and dibromohydrocinnamic acids.

[With MARIE REIMER.]—When oxidised with potassium permanganate in acetone solution, methyl α -nitrophenylcinnamenylacrylate yields dibromohydrocinnamic acid, *p*-nitrobenzoic acid, and an acid which melts at 110—120° and may be phenylbromolactic acid.

[With OSCAR LOHSE.]—Cinnamaldehyde neither reacts in presence of sodium ethoxide with a methyl group except in the cases of acetone and acetophenone, nor with methylene unless it is combined with two nitrile groups or with one nitrile and one other slightly acid group. Other aldehydes also take part in the reaction. The following new substances prepared by this reaction are described:

α -Cyanocitrylideneacetic acid, $C_{13}H_{17}O_2N$, obtained by the action of citral on ethyl cyanoacetate, and hydrolysis of the product, forms small, yellow crystals and melts at 150°.

o-Hydroxybenzylidenemalononitrile, $OH \cdot C_6H_4 \cdot CH:C(CN)_2$, obtained from salicylaldehyde and malononitrile, forms yellow crystals and melts at 183—184°.

Methoxybenzylidenemalononitrile, $OMe \cdot C_6H_4 \cdot CH:C(CN)_2$, from anisaldehyde and malononitrile, crystallises in slender, white needles and melts at 110°.

On addition of sodium ethoxide to the alcoholic solution of cinnamaldehyde and chloroacetonitrile, a precipitate of sodium chloride is formed, and a dark oil is obtained on evaporation of the alcohol.

G. Y.

Isomeric Esters of Orthoketo-acids. GUIDO GOLDSCHMIEDT and ALFRED LIPSCHITZ (*Monatsh.*, 1904, **25**, 1164—1176. Compare Abstr., 1904, i, 168; Meyer, Abstr., 1904, i, 747).—When heated with acetic anhydride, *o*-fluorenylbenzoic acid forms an *acetyl* derivative which crystallises in matted, white needles, sinters at 120°, and melts and is converted into fluorenylbenzoic anhydride at 150—160°. The oxime of the anhydride melts and decomposes at 237—238°, is insoluble in dilute aqueous potassium hydroxide, and dissolves in concentrated sulphuric acid to a lemon-coloured solution.

Fluorenonoylbenzoic acid, obtained by oxidation of *o*-fluorenylbenzoic acid with alkaline permanganate, is yellow and crystalline and melts at 248—250°. *Methyl fluorenonoylbenzoate*, $C_{20}H_{11}O_2 \cdot CO_2Me$, obtained by the action of methyl iodide on the silver salt or of methyl-alcoholic sulphuric acid on the acid, melts at 160—162° and dissolves in concentrated sulphuric acid to a lemon-yellow solution. An isomeric *methyl ester* is formed by warming the acid with thionyl chloride and treating the product with methyl alcohol; it melts at 184—186° and dissolves in concentrated sulphuric acid to a red solution. The *acetyl* derivative obtained by heating the acid with acetic anhydride melts at 178—180° and dissolves in concentrated sulphuric acid to a red solution.

Methyl naphthoylbenzoate, $C_7H_{11}O \cdot CO_2Me$, obtained by esterifying the acid with methyl alcohol and concentrated sulphuric acid or hydrogen chloride, by treatment of the silver salt with methyl iodide, or by the action of methyl alcohol on the acid chloride obtained by means of thionyl chloride, forms large, glistening, monoclinic crystals [$a:b:c = 1.3561:1:1.0897$; $\beta = 74^\circ$], melts at 117—120°, and dissolves in concentrated sulphuric acid to an intensely yellow solution which slowly becomes red. The isomeric *methyl ester* is formed by the action of methyl alcohol on the acid chloride obtained by means of phosphorus trichloride or pentachloride; it separates from methyl alcohol in monoclinic crystals [$a:b:c = 0.6138:1:1.5430$; $\beta = 67^\circ 16'$], melts at 134—137°, and dissolves, as does the free acid, in concentrated sulphuric acid to a violet solution.

Ethyl fluorenonecarboxylate, which melts at 84—86° (Abstr., 1903, i, 161), is also obtained by the action of ethyl iodide on the silver salt, by esterification with alcohol and sulphuric acid, or by treatment with alcohol of the acid chloride prepared by means of phosphorus trichloride. The *methyl ester*, $C_{13}H_7O \cdot CO_2Me$, prepared by the various methods, crystallises in glistening, yellow needles, melts at 86—89°, and dissolves, like the free acid, in concentrated sulphuric acid to a red solution. No second ethyl or methyl ester of fluorenonecarboxylic acid could be obtained. G. Y.

Isomeric Esters of Aromatic-Keto-acids. HANS MEYER (*Monatsh.*, 1904, 25, 1177—1195. Compare Abstr., 1904, i, 747; Goldschmiedt and Lipschitz, preceding abstract).—*o*-Benzoylbenzoic chloride, prepared by the action of thionyl chloride on the acid and the excess of the reagent removed by a current of dry air at 50° under reduced pressure, is a colourless, viscid oil which does not solidify when strongly cooled, or on addition of a crystal of the acid chloride which melts at 68—71°. It distils at 330—350°, decomposing into hydrogen chloride and anthraquinone, and when treated with concentrated aqueous ammonia at 0° yields the amide, which is also formed by the action of ammonia on either of the methyl esters. In the presence of aluminium chloride, the liquid acid chloride reacts with benzene to form phthalophenone.

o-Benzylbenzoic acid, prepared by Ullmann's method (Abstr., 1896, i, 563), crystallises in long needles; the silver salt crystallises in needles and, with methyl iodide, forms the methyl ester, which is also obtained by

conversion of the acid into its chloride by means of thionyl chloride and treatment of the product with methyl alcohol. It is a colourless liquid, which has a pleasant odour, and is oxidised by chromic acid to the δ -lactone of dihydroxytetraphenylethanedicarboxylic acid (Ullmann, *loc. cit.*). The esters of *o*-benzoylbenzoic acid are reduced by zinc and acetic acid to the lactone of benzhydrylbenzoic acid and a small amount of a less fusible product which contains no methoxy-group. The action of phenylhydrazine on the isomeric esters, in absence of a solvent, leads to the formation of Roser's phenylhydrazone (Abstr., 1885, 797), which melts at $162\text{--}163^\circ$ instead of at $180\text{--}182^\circ$, as stated by that author.

Methyl *p*-toluoyl-*o*-benzoate, obtained by the action of alcohol and sulphuric acid on the acid, or of methyl sulphate on the potassium salt, melts at 61° ; previous authors have given the melting point as 54° and 66° . The isomeric *methyl ester*, formed by the action of methyl alcohol on the liquid acid chloride, which is obtained by means of thionyl chloride, melts at $71\text{--}72^\circ$, is less soluble than its isomeride, and gives an intensely yellow coloration with concentrated sulphuric acid. A mixture of equal amounts of the two isomeric esters melts at $48\text{--}49^\circ$.

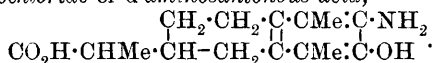
Methyl p-hydroxybenzoylbenzoate, formed by the action of sulphuric acid and methyl alcohol on the acid, melts at 134° . The isomeric *ester* obtained by the thionyl chloride method melts at $134\text{--}135^\circ$ and dissolves in concentrated sulphuric acid to an intensely orange-yellow solution. A mixture of the two esters melts at $112\text{--}114^\circ$.

The methyl ester of tetrachlorobenzoylbenzoic acid, which is obtained by shaking the potassium salt with methyl sulphate in aqueous solution, crystallises in needles and melts at 92° . The chloride formed by the action of thionyl chloride on the acid is crystalline, melts at $179\text{--}180^\circ$, and, when boiled with methyl alcohol, yields the second methyl ester, which crystallises from a mixture of chloroform and methyl alcohol and melts at 154° (Kircher, Abstr., 1887, 831).

The action of diazomethane on *o*-benzoylbenzoic, *p*-toluoyl-*o*-benzoic, and tetrachlorobenzoylbenzoic acids leads to the formation of the more fusible methyl esters. It is probable that the free *o*-keto-acids and their more fusible esters, which are therefore the ψ -esters, have the lactonic constitution.

G. Y.

Introduction of Nitrogen into the Santonin Molecule, and the Physiological Behaviour of Certain Santonin Derivatives. EDGAR WEDEKIND (*Zeit. physiol. Chem.*, 1904, 43, 240—248. Compare Abstr., 1904, i, 60).—Benzene azodesmotroposantonin (Abstr., 1903, i, 542), on reduction with stannous chloride and hydrochloric acid, yields the *hydrochloride* of *d*-aminosantonous acid,



It crystallises in plates, which tend to turn red on exposure to the air, is dextrorotatory, and its aqueous solutions have a strong acid reaction. The *amino-acid* crystallises from alcohol in colourless needles, melting at 206° , and is only sparingly soluble in water.

Santonin, desmotroposantonin, santononic acid, and the above hydro-

chloride have been examined from a physiological point of view. Although santonin acts as a strong poison when taken into the human system, none of these four compounds has any appreciable toxic effect on lower animals, and only santonin itself appears to be capable of destroying ascarides.

J. J. S.

Glycollic Acid Derivatives of Pyrogallol and its Alkyl Ethers.

AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 155568).—Pyrogallol and its alkyl ethers combine with chloroacetic acid on boiling with sodium hydroxide in a reflux apparatus or in an open vessel, the volume of the solution being maintained constant. The condensation product separates on acidifying with hydrochloric acid, and may be recrystallised from water.

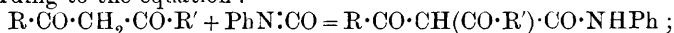
Pyrogallolglycollic acid, $C_6H_3(OH)_2 \cdot O \cdot CH_2 \cdot CO_2H$, melts at $153-154^\circ$ and dissolves readily in alcohol or hot water, sparingly in cold water, ether, or benzene; the alkaline solution becomes brown in air. *Pyrogalloldiglycollic acid*, $OH \cdot C_6H_3(O \cdot CH_2 \cdot CO_2H)_2$, is similar, but its alkaline solution does not darken in air.

Pyrogallol ethyl ether diglycollic acid, $OEt \cdot C_6H_3(O \cdot CH_2 \cdot CO_2H)_2$, crystallises from benzene and melts at $108-109^\circ$; *pyrogallol diethyl ether glycollic acid*, $C_6H_3(OEt)_2 \cdot O \cdot CH_2 \cdot CO_2H$, melts at $82-83^\circ$. The poisonous character of pyrogallol disappears in these derivatives. C. H. D.

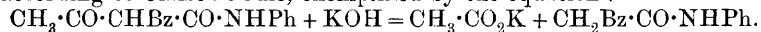
Decomposition of Gallotannic Acid. FRANZ UTZ (*Chem. Zeit.*, 1905, 29, 31).—When tannin is boiled with dilute hydrochloric acid, dextrose is first formed and, on further boiling, lævulose and furfuraldehyde.

A. McK.

Interaction of Paenylcarbimide with 1:3-Dicarbonyl Compounds. WALTER DIECKMANN, J. HOPPE, and RICHARD STEIN (*Ber.*, 1904, 37, 4627—4638. Compare Abstr., 1904, i, 847, 873).—The majority of acyclic 1:3-dicarbonyl compounds, for example, ethyl benzoylacetate, acetylacetone, benzoylacetone, dibenzoylmethane, and ethyl malonate, interact with phenylcarbimide giving *C*-carbanilides, according to the equation:



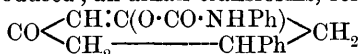
that the products are not *O*-carbanilides, as has been assumed previously in several cases, for instance, those of dibenzoylmethane and benzoylacetone, is shown by the fact that they have an acid character, give the ferric chloride reaction, and are hydrolysed according to Claisen's rule, exemplified by the equation:



These *C*-carbanilides, however, are produced either at the ordinary temperature or at 100° only in presence of traces of alkali, for example, that imparted by soda-glass. In the case of alkyl-substituted ethyl acetoacetates and acyclic 1:3-diketones, the interaction with phenylcarbimide, even in presence of alkali, takes place extraordinarily slowly, but traces of a *C*-carbanilide appear to be formed.

In all these cases, the formation of an *O*-carbanilide could not be detected. On the other hand, the dihydroresorcinols, like phenols in absence of alkali, give at once *O*-carbanilides; the hydroxymethylene-compounds, however, although giving *O*-carbanilides, require the pre-

sence of traces of alkali to initiate the action. When an alkali is used in the case of the dihydroresorcin, instead of getting an *O*-carbanilide, a *C*-carbanilide is produced; an alkali transforms, for instance,



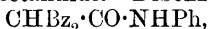
into $\text{CO} \begin{array}{c} \text{C(CO}\cdot\text{NHPh):C(OH)} \\ \text{CH}_2 \text{-----CHPh} \end{array} \text{CH}_2$, in a few minutes at 100° . The analogous transformation of the *O*-carbanilide of hydroxymethylene acetophenone into the *C*-carbanilide, $\text{CHBz}\cdot\text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh} \rightarrow \text{OH}\cdot\text{CH}\cdot\text{CBz}\cdot\text{CO}\cdot\text{NHPh}$, can be effected by heating it in ethereal solution with dry potassium carbonate. In the case of phloroglucinol, no interaction with phenylcarbimide occurs at 100° when an alkali is absent; the addition of a trace of sodium carbonate gives rise to a substance which, differing from Goldschmidt's tricarbanilide, is undoubtedly the *O*-tricarbanilide.

These facts show that the use of phenylcarbimide in ascertaining the structure of isodynamic substances is subject to considerable limitations. The new compounds obtained in investigating the foregoing cases are as follows:

Ethyl benzoylmalonanilate, $\text{OH}\cdot\text{CPh}\cdot\text{C(CO}_2\text{Et)}\cdot\text{CO}\cdot\text{NHPh}$, obtained from ethyl benzoylacetate and phenylcarbimide, crystallises from alcohol in colourless needles and melts at $142\text{--}143^\circ$; on hydrolysis with alcoholic potassium hydroxide, it gives benzoic acid and malonanilic acid.

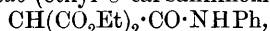
Ethyl acetylbenzylmalonanilate, $\text{CH}_2\text{Ph}\cdot\text{CAc(CO}_2\text{Et)}\cdot\text{CO}\cdot\text{NHPh}$, could not be isolated in the case of the interaction of ethyl benzyl-acetoacetate with phenylcarbimide, but its formation is evident from the fact that the product on hydrolysis gives *α*-carboxy*di*hydrocinnam-anilide, $\text{CH}_2\text{Ph}\cdot\text{CH(CO}_2\text{H)}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises from alcohol in colourless needles and decomposes on melting, giving dihydrocinnam-anilide; the latter melts at 97° , not at 92° as previously stated.

Diacetylacetanilide, $\text{CHAc}_2\cdot\text{CO}\cdot\text{NHPh}$, prepared from acetylacetone, crystallises from alcohol in colourless needles and melts at $117\text{--}119^\circ$. *Benzoylacetylacetanilide*, $\text{CH}_3\cdot\text{C(OH):CBz}\cdot\text{CO}\cdot\text{NHPh}$, obtained from benzoylacetone, forms colourless needles, melts at 126° , and on hydrolysis gives benzoylacetanilide. Dibenzoyletanilide,



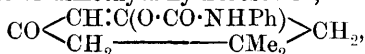
obtained by the action of phenylcarbimide on dibenzoylmethane, gives on hydrolysis benzoic acid and benzoylacetanilide.

Dicarbethoxyacetanilide (ethyl *C*-carbanilinomalonate),



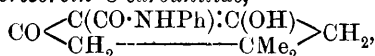
separates from alcohol in colourless crystals, melts at 122° , and, on hydrolysis, gives malonic acid monanilide.

The *O*-carbanilide of dimethyldihydroresorcin,



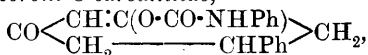
crystallises from benzene in colourless needles, melts at $105\text{--}106^\circ$, and on hydrolysis gives methyl phenylcarbamate and dimethyldihydroresorcin.

Dimethyldihydroresorcin C-carbanilide,

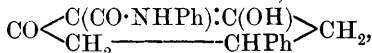


crystallises from alcohol, melts at 93—94°, and is not attacked by methyl alcoholic potassium hydroxide.

Phenyldihydroresorcin O-carbanilide,

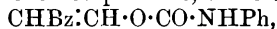


crystallises from benzene and melts between 130° and 184°, decomposing into its components. The *C-carbanilide*,



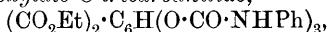
melts at 136° and is not hydrolysed by alcoholic potassium hydroxide. The isomeric *C-carbanilide*, $\text{CO} \begin{array}{c} \text{CH} \cdot \text{C}(\text{OH}) \\ \text{CH}_2 \cdot \text{CHPh} \end{array} > \text{CH} \cdot \text{CO} \cdot \text{NHPh}$, obtained from ethyl cinnamate and sodioacetoacetylanilide, crystallises from alcohol and melts at 196—197°.

From hydroxymethyleneacetophenone, the *O-carbanilide*,



is obtained; it crystallises from benzene in colourless needles, melts at 123—125°, and is easily hydrolysed into its constituents. The *C-carbanilide*, $\text{NHPh} \cdot \text{CO} \cdot \text{CBz} \cdot \text{CH} \cdot \text{OH}$, crystallises from benzene, melts at 93—94°, and is only very slowly hydrolysed by alcoholic potassium hydroxide, giving then formic acid and benzoylacetanilide.

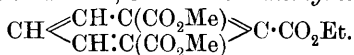
Phloroglucinol-O-tricarbanilide, $\text{C}_6\text{H}_3(\text{O} \cdot \text{CO} \cdot \text{NHPh})_3$, crystallises from alcohol or glacial acetic acid, melts at 190—191°, and is easily hydrolysed into phloroglucinol and methyl phenylcarbamate. *Diethyl phloroglucinoldicarboxylate O-tricarbanilide*,



melts at 150—155° and is also easily hydrolysed.

W. A. D.

Esterification by means of Sulphuric Acid. II. HANS MEYER (*Monatsh.*, 1904, 25, 1201—1214. Compare Abstr., 1904, i, 216).—Methyl anthranilate is formed in 92 per cent. yield when anthranilic acid is dissolved in concentrated sulphuric acid. *Methyl p-aminomesitylate*, formed by the same method, melts at 93°. *Methyl o-aminomesitylate* melts at 39° and has a slight odour resembling that of ethyl benzoate. By this method of esterification, 4 grams of hemimellitic acid yields 2.3 grams of the trimethyl and 1.2 grams of the diethyl ester. The esters were obtained in the same proportion when 5 grams of the acid were boiled with 10 grams of sulphuric acid and 50 grams of methyl alcohol (compare Graebe and Leonhardt, Abstr., 1896, i, 437; Meyer, Abstr., 1896, i, 547). When treated with thionyl chloride, dimethyl hydrogen hemimellitate is converted into its crystalline *chloride*, which melts at 84—87°, and, when treated with absolute alcohol and barium carbonate, forms the *dimethyl ethyl ester*,



This is a colourless oil, having an odour of apples, and, when shaken with *N*-sodium hydroxide solution, yields ethyl dihydrogen hemimellitate,

$\text{CH} \begin{array}{c} \text{CH} \cdot \text{C}(\text{CO}_2\text{H}) \\ \text{CH} \cdot \text{C}(\text{CO}_2\text{H}) \end{array} > \text{C} \cdot \text{CO}_2\text{Et}$, which crystallises in needles, melts at 175°, and is formed when hemimellitic anhydride is boiled with alcohol.

When dissolved in sulphuric acid and heated with methyl alcohol in a benzene-bath, mellitic acid forms the pentamethyl ester; at 100° a mixture of this with the hexamethyl ester is obtained, whilst at 120—125° the latter preponderates very largely. *Pentamethyl hydrogen mellitate* crystallises in long, silky, glistening needles and melts at 141—144°. G. Y.

Lichens and their Characteristic Constituents. IX. OSWALD HESSE (*J. pr. Chem.*, 1904, [ii], 70, 449—502, 561. Compare Abstr., 1898, i, 378, 531, 679; 1899, i, 381; 1901, i, 85, 149, 595; 1902, i, 689; 1903, i, 702).—*Cladonia squamosa* (*C. frondosa*) was gathered from a boulder in the upper Rennbach Thal near Wildbad; as with the var. *ventricosa*, the only characteristic constituent found was squamatic acid. When treated with concentrated aqueous potassium hydroxide, this acid forms delicate, white needles, probably of the potassium salt, which gradually redissolve, when, on addition of water, the solution becomes blood-red; the *barium* salt forms a white, voluminous, flocculent precipitate.

Cladonia (*Cladina*) *dstricta* contains *l*-usnic and squamatic acids, a pigment which forms a blue compound with aqueous sodium hydroxide, and an indifferent compound, *cladestin*, which forms a white, micro-crystalline powder, becomes yellow at 240°, melts at 252°, and gives a dark red coloration with ferric chloride in alcoholic solution. Zopf's *dstrictic* acid (Abstr., 1903, i, 763) was possibly squamatic acid; no trace of a colourless compound crystallising in leaflets could be found.

Cladonia furcata (*C. racemosa*, *C. recurva*) was obtained from the woods in the neighbourhood of the Waldeck Ruin, between Talmühle and Teinach stations, in Wurtemberg; it yields traces of an acid, which crystallises in small, colourless scales, and gives a red coloration with ferric chloride and a wax-like substance which is soluble in ether. *Cetraria islandica* of various origins yields proto-*a*-lichesteric acid, which is monobasic, forms the *barium* salt $(C_{18}H_{29}O_5)_2Ba$, and, when heated with hydriodic acid of sp. gr. 1.7, yields no alkyl iodide, but is almost entirely converted into a substance which melts at 70—80°; no lichesteric acid was obtained from the moss (Böhme, Abstr., 1903, i, 316). In the Iceland moss, fumaric acid is present in combination with protocetraric acid as fumaroprotocetraric acid, $C_{62}H_{46}O_{33} \cdot 2H_2O$, previously considered to be identical with protocetraric acid (Abstr., 1898, i, 534). It crystallises in small, white needles, commences to decompose at 240°, and at 260° has become black without having melted; at higher temperatures, a sublimate of fumaric acid is formed; it is sparingly soluble in water, ether, alcohol, or acetone; the alcoholic solution has an acid reaction, and gives a purple coloration with ferric chloride; in concentrated sulphuric acid, it dissolves to a dark red solution. When dissolved in aqueous alkali hydroxide, precipitated by the addition of hydrochloric acid, and again neutralised with the alkali hydroxide, fumaroprotocetraric acid is hydrolysed to fumaric and protocetraric acids, or to diethylprotocetraric acid if the reaction takes place in alcohol. Proto-

cetraric acid, $C_{54}H_{42}O_{27}$, forms spherical, crystalline aggregates, decomposes without melting at 250° , gives a purple coloration with ferric chloride in alcoholic solution, and dissolves in concentrated sulphuric acid to a red solution. The *barium*, $(C_{54}H_{39}O_{27})_2Ba_3$, the *calcium*, $(C_{54}H_{39}O_{27})_2Ca_3$, and the yellow, amorphous *silver* salt are described. When heated with methyl alcohol in a sealed tube at 100° , protocetraric acid forms the trimethyl ether, $C_{54}H_{39}O_{24}(OMe)_3$, which crystallises in short, colourless prisms, becomes black at 240° without having melted, and gives a purple coloration with ferric chloride in alcoholic solution. The *potassium* salt, $C_{57}H_{45}O_{27}K_3$, is a white powder, and on treatment with warm alcoholic potassium hydroxide forms the salt, $C_{57}H_{43}O_{27}K_5$ which crystallises in white needles. When heated with methyl alcohol and concentrated sulphuric acid in a sealed tube at 100° , trimethylprotocetraric or fumaroprotocetraric acid yields *trimethylcetrrol*, $C_{54}H_{46}O_{20}$, which forms greenish blue masses.

Dimethylprotocetraric acid, $C_{54}H_{40}O_{25}(OMe)_2$, obtained by boiling fumaroprotocetraric acid with potassium hydrogen carbonate and methyl alcohol in a reflux apparatus, forms small, yellow prisms, commences to decompose at 40° , and is blackened without melting at 260° ; it dissolves in concentrated sulphuric acid to a yellow solution which changes to blood-red. The potassium salt crystallises in small, colourless prisms.

Triethylprotocetraric acid, $C_{54}H_{39}O_{24}(OEt)_3$, is identical with cetraric acid; the potassium salt, $C_{54}H_{36}O_{24}(OEt)_3K_3$, crystallises in small, white needles.

Diethylprotocetraric acid, $C_{54}H_{40}O_{25}(OEt)_2$, obtained from fumaroprotocetraric acid, crystallises in stellate groups of white needles, and is completely decomposed, without having melted, at 250° ; the potassium salt, $C_{54}H_{37}O_{25}(OEt)_2K_3$, crystallises in white needles. *Diethylcetrrol*, $C_{51}H_{38}O_{18}(OEt)_2$, separates from water as an amorphous, flocculent precipitate, and sinters and decomposes at 250° .

Bisdiethylcetrrol, $(C_{55}H_{48}O_{20})_2$, formed along with diethylcetrrol by the action of alcoholic sulphuric acid on fumaroprotocetraric acid, is a dark blue substance, which, when heated to high temperatures, burns without previous melting, and dissolves in aqueous sodium hydroxide to a yellow solution.

The acid previously obtained from *Parmelia saxatilis* var. *sulcata* and *panniformis* (Abstr., 1901, i, 151), and termed protocetraric acid, neither yields fumaric acid when sublimed nor alkylcetrrols when heated with alcoholic sulphuric acid; it is to be distinguished as *parmatic acid*. Contrary to Zopf's statement (Abstr., 1901, i, 87), *Parmelia Borreri* contains atranorin as well as lecanoric acid.

Parmelia tinctorum, from Madras cinchona bark, yields lecanoric acid and atranorin.

P. perlata contains atranorin and *perlatic acid*, $C_{27}H_{27}O_9 \cdot OMe, 2H_2O$, which crystallises in small, white needles, loses $2H_2O$ at 80° , melts, when slowly heated, at $100-105^\circ$, when quickly heated, at $125-130^\circ$, gives a red coloration with bleaching powder in alcoholic solution, a dark blue coloration with ferric chloride, and dissolves in concentrated sulphuric acid to a colourless solution, which becomes greenish-brown on warming. The *potassium* salt, $C_{28}H_{29}O_{10}K, 2H_2O$, crystallises

in white prisms; the *barium*, *copper*, $(C_{28}H_{29}O_{10})_2Cu$, *silver*, $C_{28}H_{29}O_{10}Ag$, and the basic *lead*, $5(C_{28}H_{29}O_{10})_3Pb, PbO$, are described. The *ethyl ester*, $C_{27}H_{29}O_8 \cdot CO_2Et$, is obtained as a colourless, strongly refractive oil, which slowly solidifies to white needles, melts at $56-58^\circ$, and with bleaching powder in alcoholic solution gives an intensely red, with ferric chloride a dark blue, coloration.

When warmed at 85° with acetic anhydride, anhydrous perlatic acid yields *diacetylperlatic acid*, $C_{28}H_{26}O_9Ac_2$, which forms a white powder and melts at 55° . When boiled with aqueous baryta, perlatic acid forms barium carbonate and *perlaticol*, $C_{27}H_{30}O_8$, which sinters at 60° and melts at 80° .

Along with perlatic acid there occurs in *P. perlata* an acid which crystallises in small, white needles, melts at a little above 100° , gives a bluish-violet coloration with ferric chloride, red with bleaching powder in alcoholic solution, and forms an amorphous *potassium* salt.

P. caperata, from a sandstone wall, from *Castanea vesca* near Neu Schloss in Baden-Baden, and from beech trees in the neighbourhood of Solitude, near Stuttgart, yields *d-usnic*, *capraric*, and *caperatic* acids.

Sticta pulmonaria contains *stictic acid* (stictinic acid, Knop and Schnedermann, *J. pr. Chem.*, 1846, **39**, 365), and not *protocetraric acid* as previously stated (Abstr., 1898, i, 681).

Stictic acid, $C_{18}H_{11}O_8 \cdot OMe$, crystallises in small, yellow needles containing 2—6 per cent. of water of crystallisation lost at 100° , melts and decomposes at 264° , gives a purple coloration with ferric chloride in alcoholic solution, and dissolves in sulphuric acid to an orange-coloured solution. The *potassium*, $C_{19}H_{15}O_9K$, and the *barium*, $(C_{19}H_{15}O_9)_2Ba$, salts have been analysed.

Aspicilia gibbosa yields *aspicilic acid*, which crystallises in colourless, flat needles, melts at 119° , and, with barium chloride in ammoniacal solution, gives (1) a white, flocculent precipitate *aspicilin*, which crystallises in long, colourless, glistening leaflets, melts at 150° , distils without decomposition, and dissolves in concentrated sulphuric acid to a colourless solution which becomes brown when heated, and (2) a small amount of an acid which gives a blue coloration with ferric chloride.

Traces of *atranorin* are now found along with *lecanoric acid* in *Urceolaria scruposa* var. *vulgaris*. *Sodium lecanorate*, $C_{16}H_{13}O_7Na \cdot 4H_2O$, crystallises in small, white needles.

Chiodecton sanguineum (*C. rubrocinctum*), from Bolivian calisaya bark, contains *chiodectonic acid*, $C_{14}H_{18}O_5$, which forms a scarlet, flocculent precipitate, dissolves in alcohol to a blood-red solution, decolorised by bleaching powder, and gives a black coloration with ferric chloride, and *chiodectin*, which crystallises in long needles, melts at 120° , and is neutral.

Contrary to the statements of previous authors, *Pertusaria dealbata* does not contain *orcin*. G. Y.

Some Archil Lichens and their Chromogens. OSWALD HESSE (*Ber.*, 1904, **37**, 4693—4696. Compare Abstr., 1898, i, 531).—Contrary to Ronceray's statements (Abstr., 1904, i, 897), *erythrin* (erythric acid) melts at 148° (see *loc. cit.*, and Juillard, Abstr., 1904, i, 593), and *lecanoric acid* at 166° ; the Maquenne block is evidently not

suitable for these substances. Erythrin is found in *Roccella Montagnei*, *R. fuciformis*, and *R. fructicosa* (*R. cacticola*; *R. peruensis*), but not in *R. tinctoria*, which contains lecanoric acid. Ronceray's supposed *Dendrographa leucophæa* was *R. fructicosa*.

Erythrin is not obtained from any *Pertusaria*; Ronceray's erythrin was probably lecanoric acid.

The vanillin-sulphuric acid test is not trustworthy for orcinol in the lichens.

Juillard's anhydroerythric acid and "simple erythrin" (*loc. cit.*) were impure erythric acid, to which the author assigns the formula $C_4H_6(OH)_3 \cdot O \cdot C_6H_2Me(OH) \cdot CO \cdot O \cdot C_6H_2Me(OH) \cdot CO_2H$; picroerythric acid then becomes $C_4H_6(OH)_3 \cdot O \cdot C_6H_2Me(OH) \cdot CO_2H$. G. Y.

[Sulphonic Acids of Benzaldehyde.] CHEMISCHE FABRIK VORM SANDOZ (D.R.-P. 154528).—On dissolving toluenesulphonic acids in fuming sulphuric acid and adding manganese dioxide, oxidation to the corresponding benzaldehyde-sulphonic acids takes place, the aldehydic group remaining unattacked, even when a large excess of oxidising agent is employed. Sulphur trioxide is added from time to time to take up the water formed; the product is then poured on to ice and separated by means of sodium hydrogen sulphite. The sodium salts of benzaldehyde-*p*-sulphonic and benzaldehyde-2:4-disulphonic acids are described. The salts yield white and yellow phenylhydrazones respectively, and the latter gives rise to the disulphonated leuco-base of malachite green when condensed with dimethyl- or diethyl-aniline.

C. H. D.

Preparation of Aromatic Dihydroxyaldehydes. RUDOLF SOMMER (D.R.-P. 155731).—Hydrogen peroxide oxidises aromatic monohydroxyaldehydes in the presence of ferrous sulphate to dihydroxyaldehydes. After removing the iron by means of barium hydroxide, the aldehyde is precipitated by lead acetate. The new hydroxyl group takes the ortho-position to that already present, the aldehydic group not being attacked. Thus *m*- and *p*-hydroxybenzaldehydes yield protocatechualdehyde, and salicylaldehyde yields 2:3-dihydroxybenzaldehyde, together with a small quantity of resorcydaldehyde (compare Fenton and Jones, *Trans.*, 1900, **77**, 69; Cross, Bevan, and Heiberg, *Abstr.*, 1900, *i*, 534).

C. H. D.

Cyclic Compounds. Oxidation of 2-Methylcyclohexanone. WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1904, **336**, 299—309. Compare *Abstr.*, 1903, *i*, 836).—The product of the oxidation of 2-methylcyclohexanone contains, in addition to the three acids previously mentioned (*loc. cit.*), an acid which is very soluble in water and melts at a lower temperature than does pyrotartaric acid. Bouveault and Tétry's dianilide method of separating β - and α -methyladipic acids (*Abstr.*, 1901, *i*, 364) is unsatisfactory, as, contrary to these authors' statement (*loc. cit.*), α -methyladipic dianilide, which melts at 174—175°, is slightly more soluble in alcohol than is the β -dianilide.

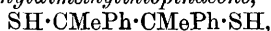
The pyrotartaric acid formed in the oxidation probably becomes inactive during the distillation, as the active anhydride, which melts

at 67—67·5°, after distillation under 760 mm. pressure melted at 42—45°, and when boiled for five minutes was completely converted into the inactive anhydride. G. Y.

Action of Ammonium Sulphide on Ketones and the Conversion of Thiopinacones into Hydrocarbons. WILHELM MANCHOT and PAUL KRISCHE (*Annalen*, 1905, 337, 170—204).—The earlier experiments of Behr, Engler, and Baumann and Fromm on the action of hydrogen sulphide or hydrosulphides on acetophenone and benzophenone is discussed. Besides repeating their experiments, the authors have investigated the reaction of ammonium sulphide on other aromatic ketones.

p-Dinitrodibenzyl ketone, prepared by nitrating dibenzyl ketone with fuming nitric acid, forms microscopic crystals melting at 105°; it is oxidised to *p*-nitrobenzoic acid by nitric acid, and gives a very delicate red coloration with alkali hydroxides. The *oxime* crystallises in needles melting at 133°, and gives a red coloration with alcoholic potassium hydroxide. The *phenylhydrazone* crystallises in needles melting at 136°. On reduction with stannous chloride, basic substances are formed, but when suspended in alcohol and treated with alcoholic ammonium sulphide containing excess of hydrogen sulphide it is converted into *p*-dinitrodibenzylthioketone, $\text{CS}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ (or the corresponding mercaptan), which crystallises in needles melting at 137°. Dibenzyl ketone is readily converted by the same reagent into tetrabenzylthiopinacone, $\text{SH}\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{SH}$, which crystallises in long needles melting at 117°.

The investigation of the action of ammonium hydrosulphide on alcoholic solutions of acetophenone led to results differing widely from those of Baumann and Fromm, who obtained two isomeric diphenylthiophens, melting respectively at 119° and 152°, whereas the authors obtained *diphenyldimethylthiopinacone*,



which forms scales melting at 118°. The substance obtained by Engler from benzophenone was found to be tetraphenylthiopinacone, and not a disulphide.

Didiphenylenethiopinacone, $\text{C}_{26}\text{H}_{18}\text{S}_2$, was prepared from diphenylene ketone (fluorenone) by treatment with alcoholic ammonium hydrosulphide, and crystallised in long needles melting at 165°.

Tetrabenzyltetramethylthiopinacone, $\text{C}_{34}\text{H}_{38}\text{S}_2$, was prepared in a similar manner from diphenylpentanone in quantitative yield; it crystallised in needles melting at 112°.

Tetrabenzylethylene, $\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{C}(\text{CH}_2\text{Ph})_2$, was obtained from the tetrabenzylthiopinacone by heating with copper powder, and fractionating the oily product, which boiled at 304°, had a faint violet fluorescence, and formed an additive product with bromine. On nitration, it yielded a tetranitrotetrabenzylethylene, $\text{C}_{30}\text{H}_{24}\text{O}_8\text{N}_4$, which crystallised in needles melting at 156°. On heating the thiopinacone for several hours at 180°, hydrogen sulphide is evolved and tetrabenzylthiopinacone formed together with sulphur.

Tetraphenylthiopinacone is converted into tetraphenylethane when heated with copper, but when heated alone into tetraphenyl-

ethylene, which crystallises in leaflets melting at 224° and does not yield a picrate, but forms a tetrabromo-derivative (m. p. 253°).

Didiphenylenethiopinacone is converted into didiphenylene-ethane (m. p. 249°) on boiling its alcoholic solution with copper powder; if the pinacone is heated directly with copper, a very small quantity of a substance crystallising in brownish-red needles and melting at 203° is obtained together with *diphenylene-ethylene*, $\text{C}_6\text{H}_4 > \text{C}:\text{CH}_2$; the latter forms orange-red crystals with an aromatic odour which melt at $104\text{--}106^{\circ}$. When heated alone at 300° , this pinacone decomposes, hydrogen sulphide being evolved, and a hydrocarbon (diphenylene-ethylene?) melting at 106° formed. Since it was possible that the formation of diphenylene-ethylene was due to the decomposition of didiphenylene-ethane, the latter was heated with copper; a small quantity of diphenylene-ethylene was produced. Since Graebe obtained didiphenylene-ethylene by distilling fluorene with lead oxide, it was probable that lead oxide could be used to remove the sulphur from didiphenylenethiopinacone, and that it would also lead to the formation of diphenylene-ethylene; such was found to be the case. Further, on heating fluorene with lead oxide, it was converted to a very large extent into diphenylene-ethylene. The diphenylene-ethylene from various sources yielded the same dibromide, $\text{C}_{14}\text{H}_{10}\text{Br}_2$, which crystallised in needles melting at 158° . When distilled with nickel in a current of hydrogen, the hydrocarbon is converted into fluorene.

K. J. P. O.

Certain Reactions of Benzoin. J. BERT. GARNER (*Amer. Chem. J.*, 1904, **32**, 583—606).—The reaction between benzoin and alcoholic potassium hydroxide or sodium ethoxide has been studied by Zinin (*J. pr. Chem.*, 1867, **98**, 495), Jena and Limpricht (*Annalen*, 1870, **155**, 93), Limpricht and Schwanert (Abstr., 1871, 536), Japp and Owens (Trans., 1885, **47**, 90), and others.

Päpcke (Abstr., 1888, 701) found that when a solution of sodium ethoxide was added to a solution of benzoin in boiling alcohol, a mass of blue crystals was produced, which became colourless when heated, but on shaking in contact with air again became coloured. On repeating this experiment, it has been found that a substance, $\text{C}_{42}\text{H}_{32}\text{O}_5\text{Na}_2$, is produced which crystallises in long, white, silky needles and is decomposed by water and most other solvents. When this compound is treated with water at 20° , benzoin, sodium hydroxide, and benzoic acid are produced. The substance is also decomposed by glacial acetic acid with formation of benzoin, benzoic acid, and sodium acetate.

On heating benzoin with alcoholic potassium hydroxide in a sealed tube for 6 hours at $150\text{--}160^{\circ}$, the following substances were obtained, the quantities stated being those produced from 16 grams of benzoin. Ethylbenzoin, 1.75 grams; hydrobenzoin, isohydrobenzoin, and their dimolecular anhydrides, 4.9 grams; benzyl alcohol, 1.9 grams; benzoic acid, 2.2 grams; benzilic acid, 0.1 gram; and ethylbenzilic acid, 4.2 grams. The last substance resembled the ethylbenzilic acid of Jena and Limpricht (*loc. cit.*), but when heated to 70° suffered violent

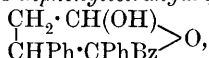
decomposition with evolution of carbon dioxide and formation of a dark red, viscous oil.

In another experiment, an alcoholic solution of benzoin was heated with sodium ethoxide for 26 hours in a reflux apparatus. The products obtained from 15 grams of benzoin were as follows: hydrobenzoin, 4.2 grams; *isohydrobenzoin*, 2.2 grams; dimolecular anhydride of hydrobenzoin, 0.8 gram; dimolecular anhydride of *isohydrobenzoin*, 0.5 gram; benzoic acid, 2.2 grams; Jena and Limpricht's so-called ethylbenzilic acid, 4.9 grams; benzilic acid, a trace; and a tetrahydrofuran derivative, 1.9 grams.

When dry oxygen is passed into a boiling alcoholic solution of benzoin and sodium ethoxide, benzaldehyde, benzoic acid, the tetrahydrofuran derivative, and traces of benzilic acid are produced.

These experiments have shown that Jena and Limpricht's so-called ethylbenzoin is a mixture of hydrobenzoin, *isohydrobenzoin*, and their dimolecular anhydrides; that the *isodesoxybenzoin* pinacone described by the same authors is a mixture of ethylbenzoin, *isohydrobenzoin*, and its dimolecular anhydride; that the so-called ethyldibenzoin obtained by Jena and Limpricht, Limpricht and Schwanert, and Japp and Owens is 2-benzoyl-2:3-diphenyl-5-hydroxytetrahydrofuran; and that the substance to which Jena and Limpricht assigned the formula $C_{28}H_{24}O$ is impure *isohydrobenzoin* dimolecular anhydride.

5-Hydroxy-2-benzoyl-2:3-diphenyltetrahydrofuran,



crystallises from hot ethyl alcohol in large, prismatic crystals, melts at 195° , and is soluble in hot benzene, ether, acetic acid, or chloroform, gives a deep red coloration with ferric chloride, and when fused with potassium hydroxide is converted into benzoic, cinnamic, and acetic acids; its *acetyl* derivative forms large, transparent plates and melts at 145° . The tetrahydrofuran compound is oxidised by chromic acid with formation of benzoic acid and carbon dioxide; it is converted by an alcoholic solution of hydrogen chloride into ethyl cinnamate and benzil. On oxidising the compound with alkaline permanganate or with nitric acid, γ -benzoyl- β -diphenylbutyrolactone is produced, which crystallises from ethyl alcohol, melts at 138.5° , and is soluble in ethyl acetate, benzene, or chloroform.

5-Hydroxy-2-benzoyl-2:3-diphenyltetrahydrofuran can also be prepared by the action of cinnamaldehyde on benzoin in presence of dilute sodium ethoxide, another substance being simultaneously produced which crystallises in needles and melts at 160 — 161° . E. G.

***o*-Benzoquinone.** RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1904, 37, 4744—4746).—*o*-Benzoquinone, $C_6H_4O_2$, is easily obtained by oxidising catechol at the ordinary temperature with freshly prepared, purified silver oxide in pure dry ether containing ignited sodium sulphate; it crystallises in dark red, transparent plates, decomposes between 60° and 70° , has no smell, and is not volatile. On reduction with sulphurous acid, catechol is at once regenerated.

W. A. D.

Action of Azoimide on *p*-Benzoquinone. RICHARD ESCALES (*Chem. Zeit.*, 1905, **29**, 31).—By the action of azoimide on *p*-benzoquinone, a *substance* is obtained which melts at 148–153°; when crystallised from ethyl acetate, the melting point is about 25° lower.

A. McK.

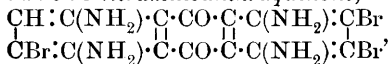
Preparation of Methylaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 156056).—Amino-derivatives of anthraquinone react with formaldehyde in strong mineral acid solution to form methylamino-derivatives. The substances may be dissolved in concentrated sulphuric acid and warmed to 55–60°. The preparation of α -methylaminoanthraquinone and of 1:6- and 1:9-dimethyldiaminoanthraquinones is described (compare Abstr., 1901, i, 839)

C. H. D.

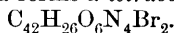
Constitution of Dibromo-1:6-diaminoanthraquinone. ROLAND SCHOLL and A. KRIEGER (*Ber.*, 1904, **37**, 4681–4686).—Scholl and Berblinger's dibromo-1:6-diaminoanthraquinone (this vol., i, 88) must be the 2:7-dibromo-compound, as the dibromotetraminoanthraquinone obtained on reduction of Scholl's dibromodinitro-1:6-dinitroaminoanthraquinone (this vol., i, 70) does not react with phenanthraquinone, and therefore cannot have amino-groups in the ortho-position to each other.

2:7-Dibromo-4:9-dinitro-1:6-dinitroaminoanthraquinone is best prepared from crude 2:7-dibromo-1:6-diaminoanthraquinone, and is purified by treatment with alcohol and hydrogen chloride, and recrystallisation from dilute ammonia.

2:7-Dibromo-1:4:6:9-tetraminoanthraquinone,

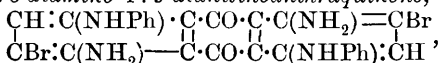


is obtained by reduction of 2:7-dibromo-4:9-dinitro-1:6-diaminoanthraquinone with aqueous potassium sulphide, or of the ammonium salt of the dinitroamino-compound with hydrogen sulphide or phenylhydrazine in aqueous solution. It crystallises in violet, glistening needles, does not melt at 360°, is insoluble in solvents of low, but sparingly soluble in those of high, boiling point, dissolves in concentrated sulphuric acid to a brown solution, which becomes red, and finally blue on dilution, and forms a *tetrabenzoyl* derivative,



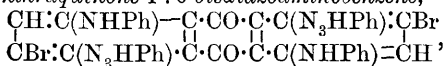
G. Y.

Action of Aromatic Bases on the Nitroamino-groups of 2:7-Dibromo-4:9-dinitro-1:6-dinitroaminoanthraquinone. ROLAND SCHOLL and A. KRIEGER (*Ber.*, 1904, **37**, 4686–4692. See foregoing abstract).—When boiled with aniline, 2:7-dibromo-4:9-dinitro-1:6-dinitroaminoanthraquinone yields azophenine and 2:7-dibromo-1:6-diamino-4:9-dianilinoanthraquinone,



which crystallises from nitrobenzene in blue needles, dissolves in cold, concentrated sulphuric acid to a violet-blue solution, and, when

warmed with sulphuric acid, forms a *sulphonic acid*, which dissolves in water and dyes wool a greenish-blue colour. When heated with aniline on the water-bath, the dinitroamine yields 2:7-dibromo-4:9-dianilinoanthraquinone-1:6-bisdiazoaminobenzene,



which forms a bluish-green powder, melts on the boiling water-bath, and resolidifies to a violet, glistening mass, unmelted at 300°, and aminoazobenzene.

2:4-Dibromo-1:6-diamino-4:9-di-*p*-toluidinoanthraquinone, formed by the action of boiling *p*-toluidine on the ammonium salt of the dinitroamine, crystallises in microscopic, blue needles.

The action of boiling dimethylaniline on the ammonium salt of the dinitroamine, leads to the formation of 2:7-dibromo-4:9-dinitroanthraquinone-1:6-bisazoxydimethylaniline, which crystallises in blue, ball-like aggregates and yields 2:7-dibromo-4:9-dinitro-1:6-diaminoanthraquinone when strongly heated or when boiled with nitrobenzene. .

G. Y.

Sulphonic Acids of *p*-Aminohydroxyanthraquinones. FARBFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 155440).—The introduction of a *p*-hydroxy-group into α -amino- or α -alkylamino-anthraquinones by the action of fuming sulphuric acid (Abstr., 1904, i, 1032) is also applicable to the sulphonic acids of those compounds. The preparation of 1-amino-4-hydroxy-7-sulphonic acid and its *methyl* and *ethyl* derivatives is described.

C. H. D.

A New α -Sulphonic Acid of Purpurin. FARBFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 155045).—Anthraquinone- α -sulphonic acid (Abstr., 1904, i, 513) is converted by fuming sulphuric acid into a new *purpurin- α -(6- or 9)-sulphonic acid*. A sulphuric ester is first formed, and may be salted out by means of potassium chloride, and this intermediate product is then hydrolysed to purpurin- α -sulphonic acid by dissolving in hot potassium hydroxide, acidifying with hydrochloric acid, and boiling. The alkali salts are red in colour.

C. H. D.

[**A New Purpurinsulphonic Acid.**] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 154337).—Anthraquinone- β -sulphonic acid is converted by concentrated sulphuric acid containing a mercury salt and arsenic or phosphoric and nitrous acids into a new *purpurinsulphonic acid*, which differs from the products obtained by direct sulphonation of purpurin. The acid dissolves in water to a red solution, from which it is precipitated by mineral acids; the alkaline solutions are red. Soluble dyes, containing the sulphonic acid group, are obtained on heating the acid with aromatic amines at 120–190°, with or without the addition of condensing agents. The products are mixtures of compounds containing one and two amine residues.

C. H. D.

Dialkyl Ethers of Anthrachrysone Derivatives. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 155633. Compare Abstr., 1903, i, 840).—The nitro- and halogen derivatives of anthra-

chrysones react with methyl sulphate to form ethers, only two methyl groups being introduced.

Dinitroanthrachryson dimethyl ether is a yellow, crystalline powder, insoluble in most solvents and melting above 300° . *Diaminoanthrachryson dimethyl ether*, obtained by reduction of the dinitro-compound, is blue in colour.

Tetrabromoanthrachryson, prepared by the addition of bromine in excess to an aqueous solution of anthrachrysonedisulphonic acid, is an insoluble, orange powder; the *dimethyl ether* forms an insoluble, orange, crystalline powder. C. H. D.

α -Derivatives of Geraniol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 154656. Compare Abstr., 1904, i, 842).—The compounds obtained from citral and magnesium alkyl or aryl haloids may be decomposed by means of concentrated organic acids instead of dilute mineral acids. The preparation of α -methyl- and α -ethyl-geraniols is described. C. H. D.

Terpenes and Ethereal Oils. LXX. Compounds of the Thujone Series. OTTO WALLACH (*Annalen*, 1904, 336, 247—280. Compare Abstr., 1893, i, 105; 1895, i, 619; 1897, i, 246; 1902, i, 801; 1903, i, 103; 1904, i, 104).—[With E. BÖCKER.]—Thujone is obtained in two chemically identical, but physically isomeric, modifications, which are best obtained in a state of purity by conversion into their semicarbazones and hydrolysis of these by means of phthalic anhydride.

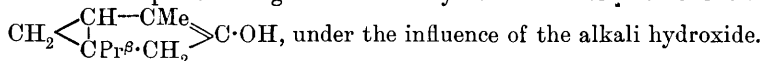
α -Thujone has $[\alpha]_D - 10.23^{\circ}$; it forms a laevorotatory, oily oxime and two semicarbazones, the one of which crystallises in rhombic prisms $[a:b:c = 0.7157:1:0.4895]$, melts at $186-188^{\circ}$, has $[\alpha]_D + 59.5^{\circ}$, and is only slightly soluble in cold ether or methyl alcohol; the other semicarbazone is amorphous, melts at about 110° , and has $[\alpha]_D$ approximately the same as the crystalline modification, than which it is more easily hydrolysed. α -Thujone is partially converted into the β -modification by warm alcoholic potassium hydroxide; it is transformed completely into β -thujone, and afterwards into isothujone by alcoholic sulphuric acid.

β -Thujone has $[\alpha]_D + 76.16^{\circ}$; it forms a crystalline oxime which melts at $54-55^{\circ}$ and has $[\alpha]_D + 105.1^{\circ}$, and a dimorphous semicarbazone which has $[\alpha]_D + 215.76^{\circ}$ to $+ 221.47^{\circ}$; the hexagonal modification $[a:c = 1:4.063]$, obtained on rapid cooling of the methyl-alcoholic solution, melts at $174-175^{\circ}$, and in solution at the ordinary temperature gradually changes into the stable modification, which crystallises in rhombic prisms $[a:b:c = 0.252:1:0.705]$, melts at $170-172^{\circ}$, has a sp. gr. 1.11 at 25° , and is more easily soluble in methyl alcohol than the crystalline semicarbazone of α -thujone.

Both α - and β -thujones yield α -thujaketonic acid, which has $[\alpha]_D + 191.99^{\circ}$ when oxidised with potassium permanganate. At certain temperatures and concentrations, solutions of the semicarbazones of α - and β -thujones deposit mixed crystals of varying melting points, especially a form which crystallises in needles and melts at $150-152^{\circ}$.

As β -thujone also is converted into a mixture of α - and β -thujones when warmed with alcoholic potassium hydroxide, these two modifica-

tions differ only in regard to the asymmetric carbon atom to which the methyl group is attached, and the conversion of one into the other takes place owing to momentary formation of the enol-form,



Oil of thuja contains principally α -thujone, oil of tansy principally β -thujone, in each case with traces of the other modification; oil of absinth contains β -thujone with smaller quantities of the α -form, whilst the oils of sage and of *Artemisia Barrelieri* contain the two modifications in about equal amounts.

[With W. FRITZSCHE.]—The oxime of β -thujone, when treated with benzoyl chloride according to the Schotten-Baumann method, yields a *benzoyl* derivative which separates from methyl alcohol in colourless crystals and melts at 52–53°. The action of phosphorus pentachloride on the oxime in chloroform solution leads to the formation of the *isooxime*, which melts at 90°, boils at 155–175° under 11 mm. pressure, and is reduced by sodium and alcohol to the secondary base, $\text{C}_{10}\text{H}_{19}\text{N}$. This forms a *nitrosoamine*, $\text{C}_{10}\text{H}_{18}\text{N} \cdot \text{NO}$, which melts at 55–56°. The *platinichloride* of the base, $(\text{C}_{10}\text{H}_{18}\text{NMe}_2\text{Cl})_2\text{PtCl}_4$, was analysed.

When acted on by benzoyl chloride in alkaline solution, the oxime of *isothujone* yields a *benzoyl* derivative, $\text{C}_{10}\text{H}_{16}\text{ONBz}$, which crystallises in needles and melts at 139–140°. With hydrogen chloride in ethereal solution, *isothujoneoxime* forms the crystalline hydrochloride, $\text{C}_{10}\text{H}_{17}\text{ON} \cdot \text{HCl}$. *isoThujoneamine*, obtained by reduction of the oxime, forms a *benzoyl* derivative, $\text{C}_{10}\text{H}_{18}\text{NBz}$, which melts at 127–128°. When reduced with sodium in alcoholic solution, the oxime yields 56 per cent. of *isothujoneamine*, the remainder being converted into *isothujone* with evolution of ammonia.

The *benzoyl* derivative of thujamenthone, $\text{C}_{10}\text{H}_{18}\text{ONBz}$, melts and decomposes at 135–136°. The liquid product obtained in the thujamenthone oxime is now shown to be a mixture of the oxime with the *isooxime*. When oxidised with potassium permanganate in warm aqueous solution, the *isooxime* yields hydroxythujamenthone *isooxime*, $\text{CHPr}^\beta \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{OH}$
 $\begin{array}{c} | \\ \text{CH}_2 - \text{CO} - \text{NH} \end{array}$, which melts at 173–174°, and *isopropyl-lævulic acid*. When the hydroxy*isooxime* is boiled with 20 per cent. hydrochloric acid, it is converted into thujamenthoketonic acid.

G. Y.

Essential Oil of the Wood of Thuja Articulata of Algeria. EMILIE GRIMAL (*Compt. rend.*, 1904, 139, 927–928).—The essential oil of the wood of *Thuja articulata* contains carvacrol, thymoquinol, and thymoquinone.
 N. H. J. M.

Condensation Product from Hæmatoxylin and Formaldehyde. ROBERTO LEPETIT (D.R.-P. 155630).—Hæmatoxylin condenses with formaldehyde on heating with acids at 100°, or without acids at 110–115° under pressure. The product is an insoluble, brownish-red powder with metallic lustre, and dissolves readily in dilute alkalis to a bluish-red solution, or in alcohol, acetic acid,

glycerol, or acetone to dark brownish-red solutions. It is tasteless and non-poisonous and possesses astringent properties. C. H. D.

Dyes of the Cyanine Series. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 155541).—The alkyl haloid compounds of methylated quinolines are oxidised in alkaline solution by potassium ferricyanide or potassium persulphate, forming dyes of the cyanine series. No similar dye is obtained from quinoline alkyl iodides, the presence of a methyl group in the quinoline ring being essential. The products dissolve in alcohol to blue solutions, and may be employed to increase the sensibility of photographic plates. The absorption-spectra of the dyes from quinaldine, lepidine, *p*-toluquinaldine, and a mixture of the latter with *p*-toluquinoline are described. C. H. D.

[**Formation of Furoyl Derivatives by means of Pyromucic Chloride.**] ERICH BAUM (*Ber.*, 1904, 37, 4756).—A correction (compare Abstr., 1904, i, 910). W. A. D.

Halogen Derivatives of Fluoran. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156333).—Dichlorofluoran may be readily prepared by heating phthalic anhydride and *m*-chlorophenol with zinc chloride. Condensation then occurs with the formation of a pyrone ring. The reaction is also applicable to the homologues of *m*-chlorophenol or *m*-bromophenol and to the halogen derivatives of phthalic anhydride.

o-Chloro-*p*-cresol (2-chloro-4-hydroxytoluene), prepared by boiling the diazonium compound of 2-chloro-*p*-toluidine, forms colourless needles melting at 55°, and boils at 228°; it dissolves very readily in alcohol or ether, and separates from water in spear-like crystals. *o*-Bromo-*p*-cresol melts at 55–56°, boils at 245–246°, and dissolves sparingly in water. 3:4-Dichlorophenol forms colourless needles; it melts at 64–65° and boils at 145–146°.

Tetrachlorofluoran, from dichlorophenol and phthalic anhydride, melts at 255°; dichlorodimethylfluoran forms small, colourless crystals and melts at 285°; dibromodimethylfluoran melts at 284–285°.

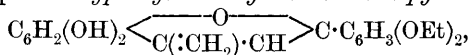
C. H. D.

Ethylacetylacetone and its Condensation Products with Polyvalent Phenols. CARL BÜLOW and IVO DEIGLMAYR (*Ber.*, 1904, 37, 4528–4531. Compare Bülow, Abstr., 1903, i, 272; Bülow and Deiglmayr, Abstr., 1904, i, 609).—When hydrogen chloride is passed into a solution of methylacetylacetone and resorcinol in glacial acetic acid containing a little acetic anhydride, ether being added when the dark brown mass becomes viscous, glistening, greenish-yellow crystals of the hydrochloride of 7-hydroxy-2-methyl-3-ethyl-4-methylene-1:4-benzopyran,
$$\text{OH} \cdot \text{C} = \text{CH} \cdot \text{C} \cdot \text{O}(\text{HCl}) \cdot \text{CMe} \\ \text{CH} : \text{CH} \cdot \text{C} \cdot \text{C}(\text{CH}_2) \cdot \text{CEt}$$
, separate. The picrate, prepared by adding picric acid to a boiling alcoholic solution of the hydrochloride, crystallises in yellow needles and dissolves in concentrated sulphuric acid to a yellow solution with slight blue fluorescence.

The constitution of 7-hydroxy-2-methyl-3-ethyl-4-methylene-1:4-

benzopyran was proved by the isolation of methyl propyl ketone, resacetophenone, and acetic acid from the products of the action of potassium hydroxide on the hydrochloride. C. H. D.

Three Position Isomeric Hydroxyl Derivatives of Resacetin. CARL BÜLOW and CONSTANT SAUTERMEISTER (*Ber.*, 1904, **37**, 4715—4723. Compare Abstr., 1904, i, 262, 609, 610).—The *hydrochloride* of 5:7-*dihydroxy*-2-*op-diethoxyphenyl*-4-methylene-1:4-benzopyran,



is obtained by the condensation of diethoxybenzoylacetone with phloroglucinol in acetic acid solution, and in presence of hydrogen chloride at 30—40°. It crystallises from a mixture of alcohol, water, and concentrated hydrochloric acid in anhydrous, orange-red needles, which are hydrolysed to the base when boiled with water. The *picrate*, $\text{C}_{26}\text{H}_{23}\text{O}_{12}\text{N}_3$, crystallises in orange-red needles, is sparingly soluble, begins to melt at 216°, and is completely decomposed at 225°. The *platinichloride*, $(\text{C}_{20}\text{H}_{20}\text{O}_5)_2 \cdot \text{H}_2\text{PtCl}_6$, forms a yellowish-brown, crystalline precipitate, and the *base* itself crystallises from alcohol in small, dark reddish-brown needles, which melt and decompose at 170—180°. Its solution in concentrated sulphuric acid exhibits a feeble green fluorescence.

An isomeric 7:8-*dihydroxy*-derivative is obtained by the condensation of diethoxybenzoylacetone with pyrogallol; it crystallises in violet-black, glistening needles containing $1\text{H}_2\text{O}$, is moderately soluble in most organic solvents, and melts and decomposes at 196—201°. The *hydrochloride* crystallises in dark red needles, the *sulphate*, $\text{C}_{20}\text{H}_{20}\text{O}_5 \cdot \text{H}_2\text{SO}_4$, forms dark red, glistening needles melting at 236—242°, and its solution in concentrated sulphuric acid does not fluoresce. The *picrate* decomposes at about 215°, and the *diacetyl* derivative, $\text{C}_{24}\text{H}_{24}\text{O}_7$, crystallises in orange-red plates, very sparingly soluble in the usual solvents.

The 6:7-*dihydroxy*-derivative, obtained from hydroxyquinol, crystallises from alcohol in garnet-red, quadratic plates with a blue lustre, melts and decomposes at 198—211°, is readily soluble in most organic solvents, and its solution in concentrated sulphuric acid exhibits a deep green fluorescence. The *hydrochloride* crystallises in golden-yellow, glistening needles containing $1.5\text{H}_2\text{O}$. The *picrate* also forms golden-yellow crystals which melt and decompose at 195—208°. The *sulphate* forms glistening, brown needles which melt at 204—214°, and the *diacetyl* derivative forms dark red, glistening needles melting at 235—250°. Its solution in sulphuric acid does not fluoresce.

The dyeing properties of the 5:7- and 7:8-*dihydroxy*-compounds have been tested. J. J. S.

Influence of Alkaloids on Certain Processes of Oxidation. E. FEDER (*Arch. Pharm.*, 1904, **242**, 680—704).—It is known that certain metallic salts (namely, copper sulphate, mercuric chloride, silver nitrate, ferric chloride, gold chloride, and platinum chloride) are able to oxidise the solutions of certain organic substances (namely, guaiacum resin or guaiaconic acid, aloin, indigocarmin, pyrogallol, catechol,

quinol, oreinol) with production of a coloration. This action, often slow in itself, is frequently much accelerated by the presence of an alkaloid. The influence of many alkaloids in this direction has been investigated; for details, the original paper must be consulted.

The influence of alkaloids on the reduction of copper salts by dextrose and on the biuret reaction has also been examined.

C. F. B.

A New Series of Bases derived from Dihydroberberine. MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, 37, 4673—4679. Compare Abstr., 1904, i, 915).—In addition to berberinal, the salts of berberine also react with magnesium alkyl or aryl haloids yielding α -derivatives of dihydroberberine. α -Benzylidihydroberberine forms a *hydrochloride*, $C_{27}H_{25}O_4N, HCl$, crystallising from alcohol and ether and melting at 165 — 166° . The *methiodide* separates from alcohol as a yellow, crystalline powder and sinters at 170° and decomposes at 181 — 182° .

α -Methyldihydroberberine, from berberine hydrochloride and magnesium methyl iodide, separates from dilute alcohol in yellow crystals and melts at 134 — 135° . The *hydriodide* separates from dilute alcohol in bright yellow leaflets and melts at 249° ; the crystalline *hydrobromide* rapidly darkens.

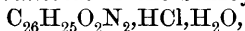
α -Phenyldihydroberberine is precipitated by ammonia from its solution in alcohol and acetic acid in brownish-yellow, glistening tablets melting at 195° .

C. H. D.

Normal Quinine Hydrochloride. CARLO ERBA (*J. Pharm. Chim.*, 1904, [vi], 20, 550—551).—The author draws attention to his study of the subject published in the *Boll. farm.*, 1901. According to his observations, the salt crystallises from 95 per cent. alcohol, is hydrated, and has the formula $C_{20}H_{24}O_2N_2, 2HCl, C_6H_6O, H_2O$, whilst Carette (Abstr., 1904, i, 1044) stated that it contained 1.5 mols. of alcohol.

G. D. L.

Constitution of β -isoCinchonicine. KARL KAAS (*Monatsh.*, 1904, 25, 1145—1152. Compare Abstr., 1900, i, 605).— β -iso- ψ -Cinchonicine is now found to be a keto-base like cinchonicine (compare Miller and Rohde, Abstr., 1894, i, 431, 432), and is therefore to be called β -iso-cinchonicine. The action of phosphorus pentachloride on β -iso-cinchonicine in chloroform solution leads to the formation of hydrogen chloride and the *hydrochloride* of a chloro-base, $C_{19}H_{21}N_2Cl, 2HCl$, which crystallises in short, yellow prisms, melts at 150° , and is hygroscopic; the chloro-base, like cinchonine chloride, does not lose chlorine when the salt is shaken with silver acetate in glacial acetic acid solution. The *hydrochloride* of the benzoyl derivative,



obtained by shaking the base with benzoyl chloride in benzene solution, crystallises in needles, melts at 228° , and is not hydrolysed when boiled with potassium hydroxide for half an hour. The action of acetic anhydride on the base leads to the formation of an oily *acetyl* derivative. When treated with methyl iodide in methyl-alcoholic

solution, β -isocinchonicine forms the *hydriodide* of the methyl base, $C_{19}H_{21}ON_2Me, HI$, which crystallises in short, yellow prisms, decomposes at 268° , and when treated successively with ammoniacal methyl alcohol and hydrochloric acid is converted into the *hydrochloride*. This is also obtained by heating β -isocinchonine methiodide with aqueous potassium hydroxide and treating the product with hydrochloric acid.

G. Y.

Creatinine. GEORG KORNDÖRFER (*Arch. Pharm.*, 1904, 242, 641—648).—The creatinine used was prepared from urine. When heated with methyl iodide and methyl alcohol, it formed a *methylcreatinine hydriodide*, $C_5H_9ON_3, HI$, melting at 212° ; the corresponding *hydrochloride*, *aurichloride* melting at 174° , *platinichloride* with $\frac{1}{2}H_2O$, and *picrate* melting at 183° were also prepared. By decomposing the hydriodide with silver oxide, the base was obtained in an amorphous state. The hydrochloride, however, could be decomposed with potassium carbonate (and therefore cannot be a quaternary ammonium salt); obtained in this way, the *base* forms crystalline, hygroscopic needles of the composition $C_5H_9ON_3, H_2O$.

The base (methylcreatinine) was heated with methyl iodide and methyl alcohol, and from the product a *dimethylcreatinine platinichloride*, $2C_6H_{11}ON_3, H_2PtCl_6$, was isolated, and also a small quantity of a salt which contained a percentage of platinum approaching that in a *trimethylcreatinine platinichloride*, $2C_7H_{13}ON_3, H_2PtCl_6$.

C. F. B.

Suprarenine [Epinephrine], the Substance of the Suprarenal Glands which causes Increase of the Pressure of the Blood. E. WEYRICH (*Chem. Centr.*, 1904, ii, 1575—1576; from *Verh. Ges. Deut. Naturfor. Aerzte*, 1903, ii, 127).—Suprarenine, prepared from fresh suprarenal glands of oxen by extracting with water which has been rendered faintly acid, forms a pale brown to yellow or greyish-white, sandy powder. The presence of extremely small crystals may be detected. Suprarenine is sparingly soluble in hot or cold water and is insoluble in alcohol or ether. The hydrochloric acid solution is emerald-green, but on the addition of dilute ammonia becomes carmine-red. The hydrochloride is precipitated by ammonia or alkali carbonates, but not by alkali acetates; it does not give any of the reactions of albumin, and its concentrated aqueous solution is not precipitated by alcohol. One gram of the base is sufficient to neutralise 0.195—0.2 gram of hydrogen chloride. The composition $C_{10}H_{15}O_3N, \frac{1}{2}H_2O$ is ascribed to suprarenine, and it is assumed to have a constitution similar to that of aminocatechol.

E. W. W.

Skimmianine, an Alkaloid from Skimmia Japonica. J. HONDA (*Chem. Centr.*, 1904, ii, 1511—1512; from *Arch. exp. Path. Pharm.*, 52, 83—94).—A poisonous alkaloid, skimmianine, has been found to be present in all parts of *Skimmia japonica*, but most abundantly in the leaves. It was isolated from the latter by extracting with 96 per cent. alcohol. *Skimmianine*, $C_{32}H_{29}O_9N_3$, crystallises from alcohol in yellow, four-sided prisms, melts at 175.5° , and is readily soluble in chloroform or alcohol, moderately so in methyl alcohol, very

sparingly so in ether, amyl alcohol, or carbon disulphide, and insoluble in water or light petroleum. All the solutions are neutral to litmus. The solutions of the base are almost tasteless, but those of the salts are very bitter. Skimmianine is only dissolved by dilute mineral acids when present in excess, and the solutions on evaporation yield the salts which crystallise in needles. When the excess of acid is neutralised by alkali carbonates, or when the salts are dissolved in water and the solutions concentrated, the base is precipitated. Even after boiling with dilute acids, skimmianine does not reduce alkaline copper solutions. A solution of the alkaloid in hydrochloric acid gives voluminous precipitates with the ordinary alkaloid reagents, and forms a *platinichloride* which crystallises in rhombic plates, and is moderately soluble in water, but only sparingly so in alcohol. The precipitate formed with gold chloride is easily decomposed. Crystals of skimmianine dissolve in concentrated sulphuric acid forming a brownish-yellow solution, which, on the addition of potassium chlorate, becomes reddish-brown. By the action of the alkaloid on Fröhde's reagent, a green coloration is formed which afterwards becomes blue; a solution of potassium permanganate in sulphuric acid becomes violet and then yellowish-brown, and concentrated nitric acid forms a yellow solution which changes to orange-red.

Injection of skimmianine into the femoral lymphatics of *Rana esculenta* or *Rana temporaria* affects the appearance of the muscles at the place of application, and renders them stiff and brittle. The neighbouring muscles are also affected by larger doses. Voluntary motion becomes sluggish, the breathing superficial, and the pupils contract. Reflex sensibility appeared as a rule to increase only in the case of *Rana esculenta*. The absolute strength, and the work performed by the muscles, were apparently diminished. The alkaloid has probably a direct action on the muscles of the heart, decreasing the pulsations and causing disturbance of the diastole. The pulse is similarly affected even when atropine has been previously administered. Intravenous injection, in the case of rabbits, causes general symptoms of poisoning. Slight poisoning is accompanied by feeble spasms. The pressure of the blood falls even when chloral has been administered, but after a time it increases again, probably owing to the compensating contraction of the peripheral vessels. Skimmianine has no effect on the secretion of urine.

E. W. W.

Pharmacological Studies on Synthetical Bases of the Piperidine Series. HERMANN HILDEBRANDT (*Zeit. physiol. Chem.*, 1904, 43, 249—289. Compare Abstr., 1900, ii, 676, and this vol., i, 80).—Dimroth's thymolmercury chloride, $C_8H_7 \cdot C_6H_2Me(OH) \cdot HgCl$ (Abstr., 1902, i, 656), does not react with formaldehyde and piperidine in the cold, but, on warming, the *methylenepiperidide* derivative, $CH \begin{array}{c} \diagup C(C_8H_7) \cdot C(OH) \\ \diagdown C(HgCl) = CMe \end{array} \rangle C \cdot CH_2 \cdot C_5NH_{10}$, is obtained. This has very much the same physiological properties as other compounds containing mercury directly attached to the benzene nucleus.

The methylenepiperidide derivative of thymotic alcohol, melting at

141° (this vol., i, 80), is very hygroscopic, and readily yields a *platini-chloride*, $(C_{17}H_{25}ON)_2PtCl_6 \cdot H_2O$, which crystallises in orange plates.

o-Thymotinipiperidide (Base 2), melting at 141°, is isomeric with *p*-thymotinipiperidide (Base 1) (Abstr., 1900, i, 676), and when taken into the animal system is eliminated as a glycuronic acid derivative, which, on hydrolysis with 8 per cent. sulphuric acid, yields the *methylated base*, $C_{17}H_{27}ON$ (Base 3), melting at 144°. This can be distinguished from Base 2 by means of its *platinichloride*, $(C_{17}H_{27}ON)_2 \cdot H_2PtCl_6$, which separates in the course of a few hours. Bases 2 and 3, but not Base 1, give characteristic thymol reactions with acetic and sulphuric acids.

p-Thymotic aldehyde and the corresponding acid and *o*-thymotic acid do not condense with piperidine and formaldehyde. When taken into the animal system, the ortho-acid is partly eliminated as such, and partly in combination with glycuronic acid. It is a much more effective poison than the para-acid, which is entirely eliminated in combination with glycuronic acid.

Dannenberg's *p*-bromothymol (Abstr., 1903, i, 338) yields a *methylene-piperidide* derivative, melting at 59°. The corresponding *o*-bromo-derivative melts at 76°. They are not poisonous, and are excreted in combination with glycuronic acid. The glycuronic acid derivatives of *o*- and *p*-thymotinipiperidides cannot be precipitated from urine by the addition of basic lead acetate, whereas the derivatives of piperidides which are physiologically inactive are readily precipitated.

Auwers and Marwedel's dibromo-*p*-hydroxy- ψ -cumyl piperidide (Abstr., 1896, i, 149) is physiologically inactive, whereas *dibromo-p-cresyl piperidide*, melting at 182°, is as active as *o*- and *p*-thymotin-piperidides.

The results of various experiments tend to show that the condensation products obtained from piperidine and phenols by means of formaldehyde exhibit an acute physiological action only when the para- or one of the ortho-positions with respect to the hydroxyl group is not substituted. The meta-position with respect to the hydroxyl has an influence on the physiological action only when both meta-positions are unsubstituted, and when the methylenepiperidine residue is adjacent. A further generalisation is that only those condensation products of piperidine with phenols and formaldehyde which have an unsubstituted ortho- or para-hydrogen atom in the benzene ring undergo methylation in the animal system; it would thus appear that it is only physiologically active compounds which undergo methylation.

The organism does not appear to be capable of introducing methyl in place of a hydrogen atom in the ortho- or para-position with respect to the hydroxyl groups, and thus forming an inactive compound, hence it is the nitrogen atom which is methylated, and the hydroxyl group reacts with the glycuronic acid, forming a compound which is physiologically inactive.

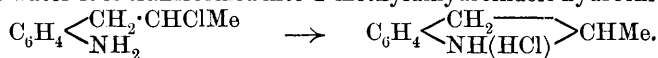
Experiments have been conducted in order to determine the effect of introducing various substituents into the piperidine ring of the condensation products.

Scholtz's *iso*-2:6-diphenylpiperidine condenses with formaldehyde and thymol when the mixture is heated, yielding a product which melts at 162°. It is physiologically inactive. 2-Methylpiperidine itself

easily volatile, has a pleasant odour, and is more easily hydrolysed than 4-cyanoquinoline. The aurichloride crystallises in needles and melts and decomposes at 158°. G. Y.

Conversion of Tetrahydroquinoline into 2-Methyldihydroindole. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1904, **37**, 4723—4730).—Tetrahydroquinoline may be transformed into 2-methyldihydroindole by means of the following reactions. Benzoyltetrahydroquinoline is converted into benzoyl-*o*- γ -chloropropylanilide (Abstr., 1904, i, 918). This is stable towards quinoline, is reconverted into the tetrahydroquinoline derivative on treatment with sodium ethoxide, but when distilled under 12 mm. pressure is mainly transformed into benzoyl-*o*-allylanilide, $\text{COPh} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2$, although benzoyl chloride and tetrahydroquinoline are formed at the same time. The benzoylallylanilide crystallises from alcohol in long needles, melts at 123—124°, and is only slowly hydrolysed by alkalis. It readily combines with hydrogen chloride when heated with three times its weight of fuming hydrochloric acid at 70—80°, yielding benzoyl-*o*- β -chloropropylanilide (this vol., i, 81).

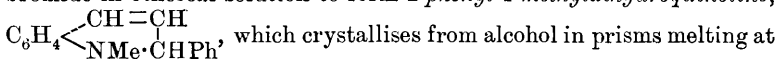
o- β -Chloropropylaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CHClMe}$, is obtained when the β -chlorinated anilide or benzoyl-*o*-allylanilide itself is heated with fuming hydrochloric acid for several hours at 125°, and when heated with water it is transformed into 2-methyldihydroindole hydrochloride :



J. J. S.

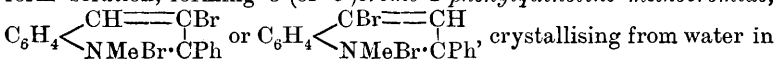
A Method for the Preparation of Compounds derived from Pseudo-bases by the Replacement of the Hydroxyl Group by Hydrocarbon Residues. MARTIN FREUND [with EDMUND SPEYER] (*Ber.*, 1904, **37**, 4666—4672).—Such salts of organic bases as yield pseudo-bases with alkali hydroxides react with magnesium alkyl or aryl haloids, forming compounds which may be regarded as derived from the pseudo-bases by the replacement of hydroxyl by a hydrocarbon residue. The reaction is a general one.

Quinoline methiodide reacts vigorously with magnesium phenyl bromide in ethereal solution to form 2-phenyl-1-methyldihydroquinoline,



and dissolves readily in acetone or chloroform, but is insoluble in water. It dissolves in hydrochloric acid, and is reprecipitated on dilution. Calcium permanganate oxidises it to benzoylmethylanthranilic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{COPh}$. Sodium reduces the base in alcoholic solution to 2-phenyl-1-methyltetrahydroquinoline, crystallising from alcohol in rhombic tablets melting at 106—107°, and possessing weak basic properties.

Bromine reacts with 2-phenyl-1-methyldihydroquinoline in chloroform solution, forming 3-(or 4-)bromo-2-phenylquinoline methobromide,



yellow needles and melting and decomposing at 248—250°. Sodium hydroxide precipitates the pseudo-base as an amorphous, yellow mass, dissolving readily in alcohol or ether. The *ammonium* base may be obtained by the action of moist silver oxide on the bromide, its aqueous solution may be evaporated without decomposition, and sodium hydroxide converts it into the insoluble pseudo-base.

The bromide decomposes on fusion into methyl bromide and 3-(or 4-)bromo-2-phenylquinoline, $C_6H_4 \begin{smallmatrix} CH: CBr \\ N = CPh \end{smallmatrix}$ or $C_6H_4 \begin{smallmatrix} CBr: CH \\ N = CPh \end{smallmatrix}$, crystallising from alcohol in white needles and melting at 120—121°.

Magnesium methyl iodide and quinoline methiodide react vigorously to form 1:2-dimethyl β -hydroquinoline, an oil becoming yellow on exposure to air and boiling at 255—256°. It dissolves readily in acids, but does not yield crystallisable salts.

Magnesium ethyl iodide and phenylacridine methiodide react to form phenylethylmethyl β -hydroacridine, $C_6H_4 \begin{smallmatrix} CPhEt \\ NMe- \end{smallmatrix} C_6H_4$, crystallising from alcohol or light petroleum in yellowish-white needles melting at 112° after sintering. The product has no basic properties.

C. H. D.

Hyposulphites of Aromatic Bases. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], 33, 67—69).—2:4-Diaminophenol hyposulphite, obtained by a mixture of molecular solutions of diaminophenol hydrochloride and sodium hyposulphite in water, crystallises in white spangles and is slightly soluble in cold water (1 in 600) and alcohol. The *hyposulphites* of diaminoresorcinol and 2:4:6-triaminophenol resemble the foregoing, but that of *p*-phenylenediamine is less stable and more soluble in water. The monoamines and pyridines also yield crystalline hyposulphites.

T. A. H.

[Indophenol from *p*-Phenylenediamine and *o*-Acetylaminophenol.] KALLE & Co. (D.R.-P. 156478).—Potassium ferricyanide oxidises a mixture of *p*-phenylenediamine and *o*-acetylaminophenol, forming a blue *indophenol*. On dissolving in sodium sulphide and passing a current of carbon dioxide, the pure *leuco-indophenol* is precipitated, and may be crystallised from organic solvents. It dissolves sparingly in water, readily in acids or alkalis. The *indophenol* yields a blue dye on fusion with sodium sulphide and sulphur.

C. H. D.

Formation of Chains. LXV. Reactions of Di- α -bromoiso-valeryldiarylethylenediamines. CARL A. BISCHOFF [and, in part, BILSEN, VON MEYSTOWICZ, PÄPKE, RADIK, ROSSI, SCHUBETSKI, TELETOFF, and WULFFIUS] (*Ber.*, 1904, 37, 4653—4666).—Di- α -bromoisovaleryldiphenylethylenediamine, from α -bromoisovaleryl bromide and diphenylethylenediamine in presence of pyridine (compare *Abstr.*, 1899, i, 278), is converted by sodium phenoxide or naphthoxide into *di-dimethylacrylodiphenylethylenediamine*, $C_6H_4(NPh \cdot CO \cdot CH: CMe_2)$, which forms

silvery needles melting at 177° and dissolving readily in chloroform, acetone, or acetic acid, less readily in alcohol or benzene.

In similar manner, di- α -bromoisovaleryldi-*o*-tolylethylenediamine yields di-dimethylacryldi-*o*-tolylethylenediamine, crystallising from alcohol in glistening needles melting at 178° . Di-dimethylacryldi-*p*-tolylethylenediamine crystallises from dilute alcohol in glistening needles and melts at 172° .

Di- α -bromoisovaleryldi- α -naphthylethylenediamine crystallises from ethyl oxalate in long, four-sided leaflets melting at 211 – 212° , and dissolves very sparingly in most organic solvents, readily in nitrobenzene. Di-dimethylacryldi- α -naphthylethylenediamine crystallises from glacial acetic acid in small, colourless prisms melting at 206 – 208° . Di-dimethylacryldi- β -naphthylethylenediamine separates from alcohol as sparingly soluble, silky needles melting at 187° , and dissolves readily in chloroform.

C. H. D.

Diamines. ADOLF LOEWY and CARL NEUBERG (*Zeit. physiol. Chem.*, 1904, 43, 355–357).—Diamines are usually isolated from urine either as benzoyl derivatives (von Udránszky and Baumann, *Abstr.*, 1889, 33, 1024) or as mercurichlorides (Brieger and Stadthagen, *Berl. Klin. Woch.*, 1889, 345). The authors employ the phenylcarbimide derivatives.

Tetramethylenediaminephenylcarbimide,



obtained by mixing the components in ethereal solution, crystallises from a mixture of pyridine and acetone in needles melting at 240° (corr.) and is insoluble in the ordinary solvents.

The corresponding derivative of *pentamethylenediamine*, $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_4$, melts at 207 – 209° (corr.) and is more readily soluble in a mixture of pyridine and acetone. The *ethylenediamine* derivative melts at 263° .

J. J. S.

Action of Secondary Asymmetric Hydrazines on Sugar. I. RUDOLF OFNER (*Monatsh.*, 1904, 25, 1153–1163. Compare *Abstr.*, 1904, i, 798, 936).—Whilst phenylmethylsazone is formed by the action of phenylmethylhydrazine on dextrose or lævulose, no osazone is formed by the action of pure *as*-phenylbenzylhydrazine on either of those substances. Neuberg's supposed lævulose-phenylbenzylsazone (*Abstr.*, 1902, i, 264) is phenylbenzylphenylsazone, which is obtained by the action of phenylbenzylhydrazine containing phenylhydrazine on dextrose or lævulose, or of pure phenylbenzylhydrazine on phenylglucosazone.

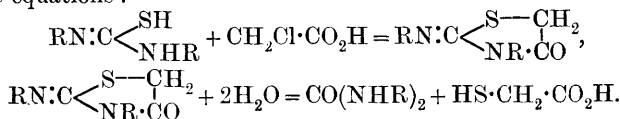
G. Y.

[Chloroindanthrene.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 155415).—A mixture of concentrated nitric acid and fuming hydrochloric acid converts indanthrene at 50° into *chloroanthraquinoneazine*, a yellow, fairly stable compound, which is reduced by sodium hyposulphite to *chloroindanthrene*, dissolving in nitrobenzene or aniline to green solutions, insoluble in water or sodium hydroxide.

C. H. D.

Study and Synthetical Preparation of Aryl Thiohydantoins.

M. EMMANUEL POZZI ESCOT (*Compt. rend.*, 1904, 139, 1031—1032).—Disubstituted ψ -thiohydantoins, readily prepared by the action of monochloro- or monobromo-acetic acid on the *s*-arylthiocarbamides (compare Abstr., 1904, i, 869), are crystalline compounds, decomposed by alkalis yielding the corresponding *s*-arylcarbamides according to the equations :



Di-o-tolyl-ψ-thiohydantoin forms slightly yellow, octahedral crystals melting 4° lower than the corresponding thiocarbamide, is slightly soluble in water and readily so in boiling alcohol or cold xylene, toluene, or chloroform. *Di-p-tolyl-ψ-thiohydantoin* crystallises from alcohol in almost colourless, small, square plates and melts at 115° . *Di-α-naphthyl-ψ-thiohydantoin* crystallises from alcohol in white prisms and melts at 183° ; the β -isomeride possesses similar properties. *Diphenyl-ψ-thiohydantoin* crystallises from alcohol and melts at 174° .

M. A. W.

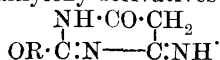
Action of Magnesium Benzyl Chloride on Crystal-violet.

MARTIN FREUND and HEINRICH BECK (*Ber.*, 1904, 37, 4679—4680).—Crystal-violet, suspended in ether, reacts vigorously with magnesium benzyl chloride to form *hexamethyltriaminotriphenylbenzylmethane*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$, separating from chloroform and alcohol in small, slightly blue crystals melting at $181\text{--}182^\circ$. Potassium iodide precipitates the crystalline *hydriodide*, melting and decomposing at $267\text{--}268^\circ$, from its solution in hydrochloric acid. No dye is obtained on oxidation with chloranil or lead peroxide and hydrochloric acid.

C. H. D.

2-Alkyloxy-pyrimidine Derivatives. FARBENFABRIKEN VORM.

FRIEDR. BAYER & Co. (D.R.-P. 155732).—The hydrochlorides of the ethers of *isocarbamide*, $\text{R}\cdot\text{O}\cdot\text{C}(\text{NH}_2):\text{NH}\cdot\text{HCl}$, prepared by the action of alcohols and hydrogen chloride on cyanamide (Stieglitz and McKee, Abstr., 1900, i, 340, 431), react with the metallic derivatives of alkyl cyanoacetates to form 2-alkyloxy-derivatives of pyrimidine,



The 2-methoxypyrimidine derivative, prepared by adding sodium to a solution of ethyl cyanoacetate and *isocarbamide* methyl ether hydrochloride in absolute methyl alcohol, crystallises from hot water or alcohol in colourless needles melting at $228\text{--}229^\circ$ and dissolving readily in alkalis or acids. The 2-ethoxy-derivative is similar, and melts at 247° .

These compounds may be converted into derivatives of hypoxanthine by Traube's method (Abstr., 1900, i, 416).

C. H. D.

Preparation of Diethylxanthine. GEORG SCARLAT (*Chem. Centr.*, 1904, ii, 1497; from *Bull. Soc. Sci. Bucarest*, 13, 155—159).—By the action of phosphorus oxychloride on the solution obtained by heating together a mixture of pyridine and cyanoacetic acid with finely powdered diethylcarbamide, the hydrochloride or phosphate of

6-imino-2 : 4-dioxy-1 : 3-diethylpyrimidine, $\text{CO} \begin{array}{c} \text{NEt} \text{---} \text{CO} \\ \text{NEt} \cdot \text{C}(\text{NH}) \end{array} \text{CH}_2$,

is obtained as a syrup. The base, prepared from the salt by evaporating with ammonia, crystallises from water in needles and melts at 137°. The isonitroso-compound, $\text{C}_8\text{H}_{12}\text{O}_3\text{N}_4 \cdot \text{H}_2\text{O}$, crystallises in small, dark red plates and is sparingly soluble in water. 5 : 6-Diamino-2 : 4-dioxy-1 : 3-diethylpyrimidine, obtained by warming the preceding compound with yellow ammonium sulphide, forms yellow crystals, and when boiled with anhydrous formic acid yields 6-amino-5-formylamino-2 : 4-dioxy-1 : 3-diethylpyrimidine, $\text{C}_9\text{H}_{14}\text{O}_3\text{N}_4$, which crystallises from absolute alcohol in white needles and is readily soluble in water or alcohol; it melts and decomposes at 235°, forming

1 : 3-diethylxanthine, $\begin{array}{c} \text{NEt} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ \text{CO} \cdot \text{NEt} \cdot \text{C} \text{---} \text{N} \end{array} \text{CH}$, with elimination of water.

Diethylxanthine crystallises from water in yellow prisms and melts at 208°.

1 : 3 : 7-Triethylxanthine, $\begin{array}{c} \text{NEt} \cdot \text{CO} \cdot \text{C} \cdot \text{NEt} \\ \text{CO} \cdot \text{NEt} \cdot \text{C} \text{---} \text{N} \end{array} \text{CH}$, prepared by the action of ethyl iodide and sodium ethoxide (2 mols.) on diethylxanthine, melts at 115° and is readily soluble in alcohol.

E. W. W.

Acetyl Derivatives of Phenylurazole. SALOMON F. ACREE (*Amer. Chem. J.*, 1904, 32, 606—611. Compare Abstr., 1902, i, 242; 1903, i, 867).—It has been shown (Abstr., 1903, i, 867) that when acetylphenylurazole, prepared by Cuneo's method (Abstr., 1899, i, 9), is treated with diazomethane, 2-acetyl-1-phenyl-4-methylurazole is produced, which melts at 94°, but after heating at 140° melts at 113—115°. The same change takes place when the substance is left for a few months at the ordinary temperature. The product melting at 113—115° is identical with the compound which was obtained by Busch (Abstr., 1901, i, 617) by the action of acetic anhydride and sodium acetate on 1-phenyl-4-methylurazole and was inadvertently stated to melt at 129°.

A few months after the first experiments had been carried out, an attempt was made to prepare a further quantity of the substance melting at 94° from the same sample of acetylphenylurazole, which still showed the same melting point (173°) as before, but only the isomeride melting at 113—115° could be obtained. Numerous experiments have been made with acetylphenylurazole prepared in various ways, but in no case has the labile form of the methyl derivative melting at 94° again been obtained. It is probable that acetylphenylurazole prepared by Cuneo's method consists of a mixture of two substances,

the labile modification, $\text{NPh}-\text{N} \begin{array}{c} \diagup \\ \text{C} \cdot \text{O} \cdot \text{NH} \end{array} \text{C} \cdot \text{O} \cdot \text{Ac}$, and the stable modification, $\text{NPh} \cdot \text{N} \text{Ac} \begin{array}{c} \diagup \\ \text{CO} \cdots \text{NH} \end{array} \text{C} \cdot \text{O}$.

The action of acetyl chloride on the silver salt of phenylurazole has been reinvestigated. It is found that acetylphenylurazole is the chief product of the reaction, a small amount of diacetylphenylurazole, which melts at 165° , also being produced. The labile diacetylphenylurazole described by Wheeler and Johnson (Abstr., 1903, i, 693) could not be obtained.

The action of ethyl iodide on silver phenylurazole has also been re-examined (compare Wheeler and Johnson, *loc. cit.*), and it has been found that 3-ethoxy-1-phenylurazole is produced together with a smaller quantity of 3:5-diethoxy-1-phenylurazole. E. G.

[Relations between Quinonehydrazones and *p*-Oxyazo-compounds.] WALTHER BORSCHÉ (*Annalen*, 1904, 336, 346).—The author had overlooked (Abstr., 1904, i, 1056) Hewitt and Pope's description of *p*-hydroxyazobenzene hydrochloride (Abstr., 1897, i, 517).

G. Y.

[Azo-compounds from 3-Hydroxydiphenylamine.] K. OEHLER (D.R.-P. 155044).—The diazonium compounds of naphthionic acid or β -naphthylamine-5:7-disulphonic acid combine with 3-hydroxydiphenylamine to form azo-compounds, which yield very fast brown dyes on treatment with chromium salts, the hydroxy-group probably occupying the ortho-position with respect to the azo-group. C. H. D.

Azo-compounds from Sulphonic Acids of α -Amino- β -naphthol. CHEMISCHE FABRIKEN VORM. WEILER-TER-MEER (D.R.-P. 155083).—Azo-compounds of acid character, yielding dark lakes with sodium dichromate or ferric acetate, are obtained on diazotising the mono- or di-sulphonic acids of α -amino- β -naphthol in the presence of organic acids only, and combining the diazo-compounds with resorcinol in alkali hydroxide solution. C. H. D.

The Copper Compound of *p*-Nitroaniline-Red. WLADIMIR SCHAPOSCHNIKOFF and V. SVIENTOSLAVSKI (*Zeit. Farb. Text. Ind.*, 1904, 3, 422—426).—The same deep brown dye is obtained by boiling *p*-nitroaniline-red with aqueous copper sulphate containing ammonia as is formed on adding a mixture of alkaline sodium β -naphthoxide, tartaric acid, and aqueous cupric chloride to diazotised *p*-nitroaniline; after suitable purification, the compound has the composition of the copper salt, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{O})_2\text{Cu}$, of *p*-nitrobenzeneazo- β -naphthol. In a similar way, the copper salt of benzeneazo- β -naphthol may be prepared. That these substances are merely the copper salts, as supposed, is shown by the fact that on decomposition with hydrochloric acid they regenerate the hydroxyazo-compounds. W. A. D.

Azodiphenylmethane : a Correction. PAUL FREUNDLER (*Bull. Soc. chim.*, 1905, [iii], 33, 80—81. Compare Abstr., 1903, i, 585).—It is shown that the substance obtained by the author by heating benzene-*o*-azobenzyl alcohol at 130° is not, as was supposed, azodiphenylmethane, but a molecular combination of azobenzene and phenylindazole. The presence of azobenzene is probably due to the formation of a hydroxylamine derivative along with benzene-*o*-azobenzyl alcohol in the condensation of nitrosobenzene with *o*-aminobenzyl alcohol and the subsequent dehydration of this. T. A. H.

***p*-Nitrobenzeneazo-*o*-tolueneneazo- β -naphthol.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 155396).—*p*-Nitrobenzeneazo-*o*-toluidine may be diazotised at 15—20°, and then yields a garnet-red azo-compound with β -naphthol. If the fabric is first treated with β -naphthol and afterwards with the diazo-solution, the dye is deposited in the fibre, and then resembles "alizarin garnet." The colour is completely removed by means of formaldehyde-sodium hydrogen sulphite. C. H. D.

Disazo-dyes from 6-Amino- α -naphthol-3-sulphonic Acid. K. OEHLER (D.R.-P. 155740).—In the preparation of disazo-compounds from 6-amino- α -naphthol-3-sulphonic acid (Abstr., 1904, i, 809), nitro-*o*-aminophenol may be replaced by chloro-*o*-aminophenol. The combination occurs more slowly than when nitro-compounds are employed, but the properties of the dyes produced are similar.

C. H. D.

Formation of Hydrogen Cyanide by the Oxidation of Proteids. R. H. ADERS PLIMMER (*J. Physiol.*, 1904, 32, 51—58. Compare Abstr., 1904, i, 538).—By the oxidation of albumins with chromic acid, a constant amount of hydrogen cyanide is evolved, which varies for each albumin; the amount thus obtained is usually greater than in oxidation by Neumann's nitric acid mixture. The products of proteolysis give a rather greater amount than the albumins themselves. The hydrogen cyanide arises from the glycine and aspartic acid, but the other amino-acids also give rise to a small quantity which, however, is negligible in comparison. W. D. H.

Amyloid. CARL NEUBERG (*Chem. Centr.*, 1904, ii, 1576—1577; from *Verh. Deut. Path. Ges.*, 1904, 19—32).—According to Krawkow, amyloid is a compound of chondroitinsulphuric acid with a proteid. The latter differs materially from the albumin of the cell, and more nearly resembles the protamines or histones. The results of the hydrolysis of a liver amyloid showed that it yielded 0.8 per cent. of glycollic acid, 22.2 of leucine, 3.8 of glutamic acid, 4.0 of tyrosine, 3.1 of pyrrolidine-2-carboxylic acid, 13.9 of arginine, and 11.6 of lysine; histidine was not present. The leucine consisted of a mixture of aminoisobutylic acid and F. Ehrlich's *isoleucine*. Complete precipitation of pyrrolidine-2-carboxylic acid from a solution in methyl alcohol may be effected by means of a solution of mercury acetate in methyl alcohol to which potassium methoxide has

been added. Since it is improbable that *d*-tyrosine is a component of amyloid or that racemisation takes place in the process of decomposition, it must be assumed that the fundamental constituent is a substance which is comparatively stable towards acids and resembles the protamines or Siegfried's kyrines. The monoamino-acids, which are only feebly combined with this substance, are liberated at once, and a portion of them is rendered inactive by the action of boiling sulphuric acid. The resemblance to the histones is supported by the fact that amyloid is always found in combination with an acid. Amyloid can no longer be regarded as a particular coagulation form of albumin. It has been shown that it is attacked by pepsin and trypsin in the ordinary way, although the action is somewhat slower than in the case of normal albuminous substances. Amyloid livers are thus subject to autolysis in the typical way, and the possibility of resorption cannot be doubted. Whilst the percentage composition of amyloids from different sources varies but little, the forms in which the nitrogen and sulphur are contained are by no means the same in each case; the latter may be present not only in the sulphate form, but also in a state of combination similar to that in which it is found in cystine. In the following table, the samples (1), (2), and (3) refer respectively to amyloids from liver, spleen, and a normal human aorta:

	C.	H.	N.	S.	Percentage of total N present as			Total S consists of	
					N in mon-amino-acids.	N in di-amino-acids.	N in amide form.	S in sulphate.	Non-oxidised S.
1	50.1	7.0	14.1	2.6	43.2	51.2	4.9	1.7	0.9
2	49.3	7.1	14.1	1.8	30.6	57.0	11.2	1.8	0.0
3	49.6	7.2	14.4	2.3	54.9	36.0	8.8	0.4	1.9

Proteids of a pronounced basic character always occur in places where normal tissue is undergoing change, and amyloid is a product of the metamorphosis of albuminous substances. Amyloids from the liver, spleen, and aorta may possibly represent different phases of the process of change which culminates in the formation of the typical liver amyloid.

E. W. W.

Preparation of Bromolecithin. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 156110).—Lecithin readily combines with bromine in chloroform solution, the amount of bromine taken up varying with the source of the lecithin employed. Lecithin obtained from egg-yolk absorbs 30 per cent. of its weight of bromine. On evaporation under reduced pressure, the product is obtained as a colourless, waxy mass. Unlike lecithin, bromolecithin is not hydrolysed by the intestinal juice.

C. H. D.

Iodo-derivatives of Lecithin. J. D. RIEDEL (D.R.-P. 155629).—Iodo-derivatives of lecithin are obtained by the action of iodine chloride, or of mixtures producing iodine chloride, on lecithin. The products dissolve readily in ether or warm alcohol, and swell in water; they may contain as much as 50 per cent. of iodine. Alkalis decompose them, yielding choline, glycerolphosphoric acid, and fatty iodoacids. The iodine is contained in the fatty acid residue. Choline yields only an unstable additive compound with iodine chloride. Products containing 5—20 per cent. of iodine find therapeutic application.
C. H. D.

Hæmocyanin. II. MARTIN HENZE (*Zeit. physiol. Chem.*, 1904, 43, 290—298. Compare Abstr., 1901, i, 783).—The distribution of the nitrogen in the hæmocyanin molecule has been determined by Hausmann's method with the following results: total = 16.09; as ammonia, 0.93; as humin, 0.43; diamide nitrogen, 4.45; and monamide nitrogen, 10.20 per cent. When hydrolysed with 33 per cent. sulphuric acid, the following products are obtained: histidine, lysine, glutamic acid, tyrosine, and leucine. Arginine could not be isolated, and a reducing sugar could not be detected among the products of hydrolysis.
J. J. S.

Velocity of Enzymatic Reactions. II. REGINALD O. HERZOG (*Zeit. physiol. Chem.*, 1904, 43, 222—227. Compare Abstr., 1904, ii, 164, 506).—Largely a reply to Henry (*Compt. rend. Soc. Biol.*, 1904, 57, 173). Further experiments are described, which tend to show that in solutions of equal viscosity the rate of inversion of sucrose by invertase is practically the same.
J. J. S.

Diastasic Coagulation of Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1904, 138, 1217—1219. Compare Abstr., 1904, i, 211, 228, 294, 374).—The diastasic coagulation of starch is only possible when the starch is in a state of liquefaction, produced either by a liquefying diastase such as amylase, or artificially, by heating under pressure. A 4.5 per cent. solution of starch is coagulated by an extract of malt which has not been heated, or by a mixture of extracts of barley, wheat, or rye which have not been heated with a malt extract which has been heated at 75°, a temperature at which the amylo-coagulase is destroyed, whilst the liquefying property of the amylase is preserved. Further, starch paste which has been liquefied by heating under pressure at 145° is coagulated by barley extract.
M. A. W.

Phenyl Derivatives of Elements of the Phosphorus Group. PAUL PFEIFFER [with IDA HELLER and H. PIETSCH] (*Ber.*, 1904, 37, 4620—4623. Compare Pfeiffer and Schnurmann, Abstr., 1904, i, 232; Pfeiffer and Truskier, *ibid.*, i, 544).—Triphenylphosphine is conveniently prepared by the action of magnesium phenyl bromide on phosphorus trichloride in ethereal solution; it crystallises from a mixture of alcohol and ether in colourless prisms or plates, and melts at 78.5°. Triphenylarsine, triphenylstibine, tri-*p*-tolylstibine, and triphenylbismuthine were all prepared, with a good yield, by a similar method.
W. A. D.

Organic Chemistry.

Action of Acetylene on Solutions of Mercuric Chloride. HEINRICH BILTZ (*Ber.*, 1905, **38**, 133—136. Compare this vol., i, 2; Hofmann, *Abstr.*, 1898, i, 635; 1899, i, 97, 485; this vol., i, 2).—A criticism of Hofmann's work and a claim for priority. G. Y.

Tetraiodoethylene and Di-iodoethylene. ERNST ERDMANN and HUGO ERDMANN (*Ber.*, 1905, **38**, 237—240).—Tetraiodoethylene is conveniently prepared in quantity by a modification of Maquenne's method (*Abstr.*, 1893, i, 449). Water is slowly allowed to drop into a well-stirred mixture of iodine, calcium carbide and benzene, the temperature being kept below 45°. The product is freed from di-iodoethylene by distillation with steam and recrystallised from benzene. The authors agree with Biltz (*Abstr.*, 1897, i, 389) that the di-iodoethylene is formed as a by-product. Unfavourable results were obtained on using tetraiodoethylene in place of iodoform in the treatment of wounds. E. F. A.

Action of Chlorine on *iso*Butylene. S. A. POGORŽELSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1129—1184).—The author's experiments, described in detail in this paper, show that the reaction between chlorine and *isobutylene* may, so far as the products first formed are concerned, be represented as follows: $m\text{CMe}_3\cdot\text{CH}_2 + n\text{Cl}_2 = \text{CMe}_3\text{Cl} + \text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CH}_2 + \text{CMe}_2\text{Cl}\cdot\text{CH}_2\text{Cl} + \text{CH}_2\text{Cl}\cdot\text{CMe}\cdot\text{CHCl} + \text{CH}_2\text{Cl}\cdot\text{CMeCl}\cdot\text{CH}_2\text{Cl} + \dots$. The first of these products, CMe_3Cl , requires for its formation the presence of hydrogen chloride, but it appears as a product of the total interaction of chlorine and *isobutylene*.

The water in presence of which the chlorination of the *isobutylene* took place was found to contain small quantities of trimethylcarbinol, *isobutenol*, and *isobutyleneglycol*. T. H. P.

Addition of Iodine Chloride to *iso*Butylene. A. W. ISTOMIN (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1199—1208).—The addition of iodine monochloride to *isobutylene*, in the cold, avoiding an excess of the latter, yields a small quantity of *isobutylene chloride*, but mainly *isobutylene chloroiodide* [β -chloro- α -iodo- β -methylpropane], $\text{CMe}_2\text{Cl}\cdot\text{CH}_2\text{I}$, which boils at 62—63° under 20—22 mm. pressure and has the sp. gr. 1.7502 at 15°/4°. On heating with methyl alcohol, it yields the ether, $\text{OMe}\cdot\text{CMe}_2\cdot\text{CH}_2\text{I}$, which boils at 69—70° under 20—22 mm. pressure or, with decomposition, at 165—166° under 760 mm. pressure. This ether reacts with magnesium in presence of a small quantity of magnesium methiodide, yielding β -dimethylthexylene- β -glycol dimethyl ether, $\text{OMe}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OMe}$, which boils at 190—192° under 780 mm. pressure and has the normal molecular weight in

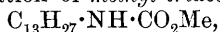
freezing benzene; when treated with hydrobromic acid, this compound yields diisocrotylic bromide (Pogorzelsky, Abstr., 1899, i, 785).

T. H. P.

Action of Water on Hexylene Dibromide (from Mannitol). HEINRICH KLARFELD (*Monatsh.*, 1905, **26**, 83—88. Compare Hecht, *Annalen*, 1881, **209**, 311).—When heated with water in a sealed tube at 160—170° for nine hours, hexylene dibromide (b. p. 91° under 17 mm. pressure) yields hexylene and a mixture of methyl butyl ketone and ethyl propyl ketone.

G. Y.

Tridecyl Alcohol. J. BLAU (*Monatsh.*, 1905, **26**, 89—109).—Myristamide (Reimer, Abstr., 1885, 1197) prepared by Aschan's method (Abstr., 1889, i, 14) melted at 105—107°, or after recrystallisation at 102°. Some preparations made with commercial phosphorus trichloride melted at 85°. The action of bromine in carbon tetrachloride solution on myristamide dissolved in methyl alcohol followed by sodium methoxide leads to the formation of *methyl tridecylcarbamate*,



which crystallises in small, white leaflets and melts at 53—54°, and myristyltridecylcarbamide, $C_{13}H_{27} \cdot NH \cdot CO \cdot NH \cdot CO \cdot C_{13}H_{27}$, which crystallises in large, silky leaflets and melts at 103°. Tridecylamine, $C_{13}H_{27} \cdot NH_2$, formed by distilling the urethane or the carbamide with potassium hydroxide, absorbs moisture and carbon dioxide from the atmosphere and solidifies to a white mass; the hydrochloride, $C_{13}H_{29}N \cdot HCl$, crystallises in small needles and decomposes at 160°; the platinichloride, $(C_{13}H_{29}N)_2 \cdot H_2PtCl_6$, crystallises in yellow spangles and decomposes at 205°, [compare Reimer and Will, Abstr., 1885, 1197; Lutz, Abstr., 1886, 685]. *Tridecyl alcohol*, $C_{13}H_{27} \cdot OH$, prepared by the action of silver nitrite and hydrochloric acid on the amine in aqueous solution, melts at 30.5°, boils at 155—156° under 15 mm. pressure, and has a sp. gr. 0.8223 at 31°/4°. On oxidation with potassium dichromate and sulphuric acid, the alcohol yields tridecoic acid, which melts at 40°.

G. Y.

Reduction of Dimethyltrimethylene Glycol ($\beta\beta$ -Dimethylpropan-*ay*-diol) by means of Fuming Hydriodic Acid. PAUL MEYERSBERG (*Monatsh.*, 1905, **26**, 41—51. Compare Apel and Tollens, Abstr., 1896 i, 115; Just, Abstr., 1896, i, 403).—When heated with an excess of fuming hydriodic acid in a sealed tube at 100—110° for about 30 hours, $\beta\beta$ -dimethyltrimethylene glycol yields the iodohydrin and *tert*-butylcarbinyl iodide (Tissier, Abstr., 1893, i, 542). The iodide distils unchanged at 42—44° under 20 mm., at 52° under 35 mm. pressure, has a sp. gr. 1.5317 at 13°, or 1.463 at 26°, and, on treatment with silver acetate in glacial acetic acid solution and hydrolysis of the product with dilute aqueous potassium hydroxide, yields *tert*-butylcarbinol. When boiled with aqueous potassium carbonate, in a reflux apparatus, the iodide yields only a small proportion of the carbinol, the remainder being converted probably into the volatile amylene.

G. Y.

Preparation of Xanthogen Compounds. L. A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1253—1258).—The preparation of xanthogen compounds by the formation of the sodium alkyloxide

and subsequent action of carbon disulphide and an alkyl iodide requires a long-continued heating of the alcohol with sodium at a high temperature, and is often accompanied by isomeric change and the formation of resinous products. The author finds that by using potassium in place of sodium the time required for the reaction is considerably shortened. The fact that primary and secondary alcohols liberate *tert.*-amyl alcohol (dimethylethylcarbinol) from potassium *tert.*-amyl-oxide may also be used to simplify the method of preparation of xanthogen compounds, as the potassium compounds of alcohols of the terpene series may be prepared in this way.

T. H. P.

Action of Dilute Acids on Pinacones. ADOLF LIEBEN (*Monatsh.*, 1905, 26, 35—39).—Contrary to what might be expected from Erlenmeyer's theory (*Ber.*, 1881, 14, 322), the results obtained by Zumpfe (Abstr., 1904, i, 291) and Kohn (following abstract) suggest that the pinacolin formation takes place with those pinacones only which contain the grouping :CMe.OH.

G. Y.

Action of Dilute Sulphuric Acid on Propionepinacone. SIEGFRIED KOHN (*Monatsh.*, 1905, 26, 111—118. Compare Zumpfe, Abstr., 1904, i, 291; Lieben, preceding abstract).—When boiled with dilute sulphuric acid for five hours in a reflux apparatus, propionepinacone yields two products.

(1) A *hydrocarbon*, $C_{10}H_{18}$, which is a colourless liquid with a pleasant odour, boils at 153° — 154° , is insoluble in water, but easily soluble in alcohol, ether, or chloroform, and forms an *additive* compound with 1 mol. of bromine.

(2) An oxide, $C_{10}H_{20}O$, which is a yellow, mobile liquid with a characteristic odour; it boils at 189° — 190° , does not form an oxime, does not react with zinc ethyl at 100° or with water at 210° — 220° , and, when oxidised with potassium permanganate in alkaline solution, yields α -ethylbutyric acid and an *acid*, $C_9H_{16}O_3$, which forms a *silver* salt, crystallising in long, white needles, and therefore is probably an $\alpha\delta$ -oxide.

G. Y.

Action of Organic Acids on Metals of the Cerium and Yttrium Groups. THEODOR H. BEHRENS (*Rec. trav. chim.*, 1904, 23, 413—418. Compare Abstr., 1902, ii, 80).—The formates of metals of the yttrium group crystallise in pentagonal dodecahedra. When aqueous solutions of the salts are evaporated at the boiling point until of syrupy consistence, they become turbid after some hours, and then, on addition of water, deposit crystals which are from 5 to 8μ long, dissolve with difficulty in water and readily in formic acid, and leave a yellow oxide on ignition. These reactions are similar to those of Marignac's terbium, the existence of which the author doubts. Erbium can be detected by examining the absorption spectrum and iron by the usual colour reactions.

When acetic acid is added to aqueous solutions of formates of the yttrium group, double salts are precipitated in the form of transparent rhombs, 30 to 50μ long, with an acute angle of 63° , optically negative

in the direction of the long diagonal, and showing well-marked colours with polarised light.

The metals of the yttrium group give salts with the aliphatic hydroxy-acids crystallising in radiating spheroids, 50 to 80 μ long, brown by transmitted light, and showing a cross when placed between the nicols. Needles 120 μ long can be obtained from dilute solutions. Metals of the cerium group as well as thorium and zirconium give readily soluble salts with these acids.

Ammonium fumarate gives precipitates of rhomboidal tablets with both the cerium and yttrium groups, the crystals in the former group being from 50 to 70 μ , and in the latter from 120 to 150 μ long. In both cases, the acute angles of the rhombs are 64–66°, and the angle of extinction 19°, but the fumarates of the yttrium group are the more soluble. Mesaconic acid gives with cerium or lanthanum nitrate spheroidal aggregates of rod-like crystals 15 μ long, and with yttrium or erbium nitrate rectangular rods 20 to 30 μ long, with angle of extinction 36° and often grouped into bunches. The mesaconates of the last two metals are more soluble than those of the former two.

T. A. H.

Preparation of Anhydrides of Chloroacetic Acids. THOMAS S. PATTERSON (*Ber.*, 1905, **38**, 210–213. Compare Buckney and Thomsen, *Ber.*, 1877, **10**, 698; Antoine, *J. Pharm. Chim.*, 1883, [v], **8**, 417; Bischoff and Walden, *Abstr.*, 1895, i, 17).—Perfectly anhydrous sodium carbonate has no action on freshly-prepared chloroacetyl chloride, but when the carbonate has been exposed to the air for a short time it reacts vigorously with the chloride yielding varying amounts of anhydride.

The following boiling points for the anhydride are given :

Pressure.....	24	36	51	62	104	116 mm.
Boiling point	126°	135°	144°	149°	161°	163°

For chloroacetic acid :

Pressure.....	18	36	68	101	152	207 mm.
Boiling point	93°	108°	121°	130·1°	140·5°	149°

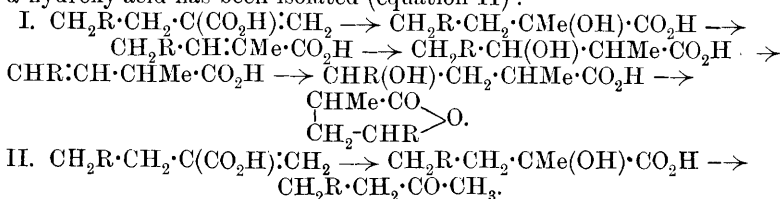
For dichloroacetic acid :

Pressure.....	21	24	36	71	88	142	164 mm.
Boiling point ...	99°	102·5°	111·5°	125°	129°	140°	144°

J. J. S.

Migration of the Ethylenic Linking in Unsaturated Open-chain Acids. EDMOND E. BLAISE and A. LUTTRINGER (*Compt. rend.*, 1905, **140**, 148–150).—Fittig has shown (*Abstr.*, 1895, i, 204) that the $\alpha\beta$ -unsaturated acids are converted by the action of alkalis into the corresponding $\beta\gamma$ -isomerides; in the present paper, the authors show that the action of concentrated or 80 per cent. sulphuric acid at 0° on the α -ethyl-, α -propyl-, α -isopropyl-, α -butyl-, α -heptyl-acrylic acids, on α -methyl- β -ethylacrylic acid, or on $\alpha\beta$ -hexenoic acid causes the ethylenic linking to migrate from the shorter into the longer carbon chain, giving an $\alpha\beta$ - or a $\beta\gamma$ -unsaturated isomeride, the latter forming

a γ -lactone (equation I). The mechanism of the reaction appears to involve successive hydrations and dehydrations, and in certain cases the ketone resulting from the decomposition of the intermediate α -hydroxy-acid has been isolated (equation II) :



When the carbon atom in the γ -position to the carboxyl groups is primary, the $\alpha\beta$ -unsaturated acid is formed, thus α -ethylacrylic acid yields tiglic acid and methyl ethyl ketone ; when the carbon atom in the β -position is tertiary, the corresponding ketone is the only product and α -isopropylacrylic acid gives methyl *isopropyl* ketone, and when the carbon atom in the γ -position is secondary, a ketone and a γ -lactone are produced.

M. A. W.

Condensation Products from Fatty Aldehydes and Negatively-substituted Acetic Acids. EMIL KNOEVENAGEL (D.R.-P. 156560).—Fatty aldehydes combine with negatively substituted acetic acids, such as malonic, cyanoacetic, acetoacetic, benzoylacetic, and acetonedicarboxylic acids in the presence of small quantities of ammonia or primary or secondary amines.

Valeraldehyde and malonic acid, with a little piperidine, yield δ -methylhexenoic acid, consisting of a mixture of the Δ^{α} - and Δ^{β} -acids, boiling at 127—132° under 25 mm. pressure. When 2 mols. of malonic acid are employed, the product is β -isobutylglutaric acid, which melts at 48° and boils at 205—210° under 15 mm. pressure. Valeraldehyde and cyanoacetic acid yield α -cyano- δ -methyl- Δ^{α} -hexenoic acid, melting at 53°, and $\alpha\alpha$ -dicyano- β -isobutylglutaric acid, melting at 162°. Heptaldehyde and malonic acid yield nonylenoic acid ; heptaldehyde and cyanoacetic acid yield $\alpha\gamma$ -dicyano- β -hexylglutaric acid, which melts at 142°. Citral also condenses with malonic or cyanoacetic acid to form citrylidene derivatives.

The condensation of aromatic aldehydes with these acids (Abstr., 1899, i, 144) requires the addition of a larger quantity of the base.

C. H. D.

Changes effected by Time on Hydrocarbon Substances of Organic Origin. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 177—183).—From the viscous fatty matter extracted from an Egyptian vase belonging probably to the XVIIIth Dynasty (B.C. 1600 to 1370), the author has isolated the acids $\text{C}_5\text{H}_{10}\text{O}_3$ and $\text{C}_4\text{H}_8\text{O}_3$ of the hydroxystearic series in the form of their soluble crystalline calcium salts, the insoluble residue consisting of a mixture of acids of the hydroxyoleic series, $\text{C}_n\text{H}_{2n-2}\text{O}_3$, and of bitumens or resins, $(\text{C}_5\text{H}_{10}\text{O})_n$; these acids are possible products of the gradual oxidation of oil of ricinus, and it is probable that this oil, together

with balms, resins, bitumens, &c., constituted the original contents of the vases. M. A. W.

Sodium Acetoacetate and the Formation of Analogous Salts in Solution. JULIUS W. BRÜHL and HEINRICH SCHROEDER (*Ber.*, 1905, 38, 220—226. Compare Abstr., 1904, i, 646, 969).—Ethyl acetoacetate was mixed with the equivalent quantity of sodium ethoxide in absolute alcohol, and the spectrochemical functions of the components of the mixture determined before and after mixing. A very great change in the dispersion takes place on mixing. Taken in conjunction with the results obtained with the esters of camphorcarboxylic acid (*loc. cit.*), it is beyond doubt that ethyl acetoacetate during salt formation is completely enolised, change taking place from a non-conjugated linking to a conjugated system:



This is discussed at some length in connection with the theory of Willstätter and Pummerer (Abstr., 1904, i, 1043) that the salts of ethyl acetoacetate with sodium ethoxide are additive compounds of the type $\text{CO}_2\text{R}\cdot\text{CH}_2\cdot\text{CR}(\text{OEt})\cdot\text{ONa}$.

It is shown, however, that the whole optical behaviour of sodium acetoacetate can only be explained on the theory that isomeric change takes place. In general, the esters of β -ketonic acids are instantly enolised when they form salts. E. F. A.

Ethyl Citrylideneacetoacetate. EMIL KNOEVENAGEL (D.R.-P. 156115).—Ethyl citrylideneacetoacetate (Abstr., 1902, i, 342) does not yield a perfume on inversion with acids. If heated for several hours at 160° with or without the addition of water, however, the ester undergoes a change, the boiling point and specific gravity being raised. On inverting the product by means of acids, a compound is obtained, boiling at 150 — 190° under 12 mm. pressure, which may be employed as a perfume. C. H. D.

Intramolecular Migration of Acyl Groups. WILHELM WISLICENUS (*Ber.*, 1905, 38, 546—548. Compare Abstr., 1901, i, 187; 1902, i, 72; Bouveault and Bongert, Abstr., 1903, i, 145; Dieckmann and Stein, Abstr., 1904, i, 873).—The author has heated ethyl *O*-acetylacetoacetate, in total absence of any alkali, in a platinum tube at 240° for three hours, and confirms the previous statement that under these conditions about 1 per cent. of the *O*-acetyl ester is converted into the *C*-derivative. G. Y.

Action of Bases on Chloral Hydrate. JOHANNES E. ENKLAAR (*Rec. trav. chim.*, 1904, 23, 419—439).—Reicher has shown that the rate of decomposition of chloral hydrate by bases is proportional to the excess of base used over that necessary to form with the chloral hydrate a salt of the type $\text{CCl}_3\cdot\text{CH}(\text{OK})\cdot\text{OH}$ (*Maandblad*, 1885, 18). The author confirms this observation, and suggests that the mechanism of the reaction is either that this salt breaks down into chloroform and a formate, or that the complex negative ion, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{O}^-$, produced by its dissociation, gives rise to chloroform

and the negative ion of formic acid, the reaction in either case being unimolecular and brought about by catalysis under the influence of the $-OH$ ions of the excess of the base used. The former explanation is considered the more probable since the reaction velocity is greater in presence of neutral salts of the base used. It is assumed that the addition of such salts diminishes the dissociation of the chloral hydrate salt and increases the total number of positive ions of the base, and that these positive ions act as accelerators of the catalysing action of the $-OH$ ions.

T. A. H.

Condensation of *n*-Butaldehyde by means of Dilute Sulphuric Acid. ADOLF GORHAN (*Monatsh.*, 1905, 26, 73—82. Compare Bauer, *Abstr.*, 1904, i, 279; Kadiera, *Abstr.*, 1904, i, 466).—When heated with 10—40 per cent. sulphuric acid at 100—200° for 8—30 hours, or when heated with fuming hydrochloric acid at 90° for four hours, or when heated in a reflux apparatus at 85—90° for eight hours, *n*-butaldehyde is partially converted into Raupenstrauch's α -ethyl- β -propylacraldehyde (*Abstr.*, 1887, 794) and an unsaturated aldehyde, $C_{12}H_{22}O_2$, which is a viscid oil and boils at 160—162° under 12 mm. pressure. It has a pleasant odour, reduces ammoniacal silver solutions, forms a crystalline precipitate with phenylhydrazine, and with bromine in chloroform solution at low temperatures yields the additive compound $C_{12}H_{22}O_2Br_2$.

G. Y.

Condensation of Formisobutaldol with Acetaldehyde. ALOIS SCHACHNER (*Monatsh.*, 1905, 26, 65—72. Compare Wessely, *Abstr.*, 1900, i, 428).—The action of formisobutaldol on acetaldehyde in presence of aqueous potassium carbonate leads to the formation of the product $OH \cdot CH_2 \cdot CMe_2 \cdot CH(OH) \cdot CH_2 \cdot COH$, which in the solid state has the bimolecular formula $(C_7H_{14}O_3)_2$ (compare Kohn, *Abstr.*, 1900, i, 274). It crystallises in sheaves of white needles, melts at 84°, is more soluble than formisobutaldol in water or the ordinary organic solvents, does not form an additive compound with bromine, and on distillation decomposes into formisobutaldol and acetaldehyde.

G. Y.

Chloromalonaldehyde. WALTER DIECKMANN and LUDWIG PLATZ (*Ber.*, 1905, 38, 339. Compare this vol., i, 117).—An acknowledgment of priority.

W. A. D.

An Isomeride of Trichloroacetone. GUSTAVE PERRIER and EUGÈNE PROST (*Compt. rend.*, 1905, 140, 146—148).—An attempt to replace the chlorine in chloral by the grouping OEt by the action of aluminium ethoxychloride, $Al_2Cl_3(OEt)_3$ (compare Perrier, *Abstr.*, 1901, i, 442), was unsuccessful, the product obtained being an isomeride of trichloroacetone, $C_3H_3OCl_3$, boiling at 182—187° under 764 mm. or at 101—103° under 30 mm. pressure, having a sp. gr. 1.423 at 15° and an odour similar to that of the terpenes. It yields chloral when warmed with sulphuric acid, chloroform when oxidised by chromic mixture, or carbylamine when heated with a mixture of potassium hydroxide, aniline, and alcohol. All these reactions show

that the three atoms of chlorine in the compound are associated with the same carbon atom, and as it differs from trichloroacetone in respect of its insolubility in water and in not being attacked by hot or cold ammonia, the authors suggest the following provisional constitutional formula for the compound $\text{CCl}_3 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{O} \end{smallmatrix}$.

M. A. W.

Chlorination of Methyl Ethyl Ketone. ANDRÉ KLING (*Compt. rend.*, 1905, 140, 312—314. Compare Vladesco, 1892, 424, 810; Reymenant, 1901, i, 126).—The action of chlorine on methyl ethyl ketone in presence of water and calcium carbonate leads to the formation of two monochloro-substitution products. The action takes place most regularly at 60—70°. At low temperatures, the action frequently only begins when a considerable quantity of chlorine has been absorbed by the solution, and there is then danger of explosion. The products of incomplete chlorination are the same when the ketone is acted on by sulphuryl chloride, by free chlorine, or by chlorine in presence of iodine, but the best results are obtained by the first method.

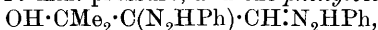
The two products can be separated by repeated fractionation. The one which boils at 40—41° under 30 mm. and at 114—117° under 760 mm. pressure is *methyl α -chloroethyl ketone*, $\text{CH}_3 \cdot \text{CHCl} \cdot \text{COMe}$. The other boils at 59—60° under 30 mm. and at 134—136° under 760 mm. pressure, and is *chloromethyl ethyl ketone*, $\text{COEt} \cdot \text{CH}_2\text{Cl}$, for on converting it into the corresponding alcohol and reducing this, the glycol, $\text{OH} \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{OH}$,

is obtained. The substance obtained by Reymenant, and stated to boil at 125°, was probably a mixture of these two substances. H. M. D.

New Method of Synthesising Saturated Ketones by Catalytic Reduction. GEORGES DARZENS (*Compt. rend.*, 1905, 140, 152—153).—Aliphatic unsaturated ketones of the type $\text{C}_n\text{H}_{2n-2}\text{O}$ are converted into the saturated ketones, $\text{C}_n\text{H}_{2n}\text{O}$, by direct hydrogenation at 180—190° in the presence of nickel obtained by reducing nickel oxide at 245—250° (compare this vol., i, 66), and the following ketones were thus prepared: methyl *isobutyl* ketone from mesityl oxide; methyl *isoamyl* ketone from methylhexenone, and methyl *isohexyl* ketone from natural methylheptenone, or from the synthetical compound.

M. A. W.

Addition of Hypochlorous Acid to Allene Hydrocarbons. II. F. W. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1184—1199. Compare Abstr., 1904, i, 214).—The action of hydrochlorous acid on unsymmetrical dimethylallene yields, as principal product, *chloromethyl hydroxyisopropylketone*, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, which boils at 84—85° under 10 mm. pressure; the *acetyl* derivative, $\text{OAc} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, forms crystals melting at 47·5° and boiling at 102—104° under 10 mm. pressure, and the *phenylosazone*,



separates from alcohol in golden-yellow crystals melting at 141°.

The other products of the reaction are: (1) chloromethyl chloroiso-

propyl ketone and (2) $\beta\beta$ -dichloro- $\alpha\delta$ -dihydroxy- γ -methylbutane,
 $\text{OH}\cdot\text{CMe}_2\cdot\text{CCl}_2\cdot\text{CH}_2\cdot\text{OH}$,

which forms crystals melting at 151° , dissolves readily in alcohol or ether, and to a less extent in benzene or water, and reduces Fehling's solution in the cold.

The above products are what would be expected, according to theory, to be formed in this reaction. T. H. P.

Birotation of Galactose. GUNNAR HEIKEL (*Annalen*, 1905, 338, 71—104).—The most probable cause of the birotation of an aldhexose is the existence of two stereoisomeric lactone forms, which are very readily transformable into one another, possibly through the intermediary stage of the aldose. This supposition has found support in the fact that pyridine solutions of dextrose of different rotatory powers yield two penta-acetates (Abstr., 1904, i, 657).

On investigating galactose, it was found that an aqueous solution had $[\alpha]_D$ 80.8° at 20° , but in anhydrous pyridine at first $[\alpha]_D$ 170° , and finally $[\alpha]_D$ 55.6° . Solid galactose, when acetylated in pyridine solution at 0° , yielded a *penta-acetate*, $\text{C}_6\text{H}_7\text{O}_6\text{Ac}_5$, which could not be crystallised and had $[\alpha]_D + 71.8^\circ$ in benzene at 20° . The already known β -penta-acetate, prepared by acetylating at the ordinary temperature, melts at 141.5 — 142° , and has $[\alpha]_D$ 59.2° , whilst an amorphous substance formed at the same time has $[\alpha]_D$ 60.8° . When the acetylation is carried out at 100° , the same β -acetate and a product having $[\alpha]_D$ 28.6° , and when the acetylation is carried out in pyridine at 50 — 60° , the β -acetate and a product having $[\alpha]_D$ 49.7° , are obtained. The acetate having $[\alpha]_D$ 71.8° is probably the pure isomeric α -acetate, whereas the other amorphous forms are taken to indicate the existence of a third, γ -acetate. The behaviour of galactose dissolved in boiling pyridine confirms this supposition, since an initial rotation of $[\alpha]_D$ 31° changes slowly into the rotation of $[\alpha]_D$ 59.26° when the solution has cooled.

It seems probable that the γ -penta-acetate corresponds with the aldehyde form of the sugar. In aqueous solution, the α -galactose with the high rotatory power changes into a mixture of the β - and γ -galactoses. At a higher temperature, the equilibrium changes in favour of the γ -galactose. Attempts to convert the penta-acetates into different methylglucosides yielded only the mixture of known glucosides. K. J. P. O.

[**Birotation of Dextrose.**] ROBERT BEHREND (*Annalen*, 1905, 338, 105—107. Compare preceding abstract).—Since Heikel has shown that at least three modifications of galactose exist, it is probable that dextrose also possesses an aldehyde form. In order to demonstrate that the birotation of dextrose is not due to hydration, dextrose was dissolved in anhydrous pyridine at 0° and the rotatory power determined after given intervals of time. The change was found to be a reaction of the first order; if it was a case of hydration, the reaction would have been one of the second order; further, it is not probable that dextrose would take up water from pyridine, which potassium hydroxide was not capable of withdrawing. K. J. P. O.

Influence of Inactive Substances on the Optical Rotation of Dextrose. INA A. MILROY (*Zeit. physikal. Chem.*, 1904, 50, 443—464).—The following substances, when added to an aqueous solution of dextrose, are found to increase the specific rotation, the dextrose solution being first kept for at least 24 hours after its preparation: phosphoric, arsenic, and boric acids, aluminium acetate, cerium sulphate, lead acetate, sodium tungstate, ammonium molybdate, methyl, ethyl, *n*-propyl, and isopropyl alcohols, acetone, acetaldehyde, and glycerol. In general, the increase of the specific rotation is approximately proportional to the amount of added substance. When methyl and ethyl alcohols are added, the rotation does not at once assume a steady value, but gradually increases with the time, becoming constant after 48—72 hours. In the case of *n*-propyl alcohol and acetone, the same phenomenon is observed only for the larger additions of these substances; when the added quantities are smaller, the rotation falls off with the time, finally reaching a constant value, which, however, is still greater than that for dextrose alone.

The following substances, added to dextrose solutions, diminish the specific rotation: potassium, sodium, and barium hydroxides, ethylamine, diethylamine, triethylamine, pyridine, borax, mercuric chloride, aniline hydrochloride, dimethylaniline hydrochloride, phenol, and pyrogallol. So far as the bases in this list are concerned, the diminution of rotation is more extensive and more rapid the stronger the base. It will be observed that in general the effect of acids is to increase, the effect of bases is to diminish, the rotation of dextrose.

The following substances are found to be without effect on the rotation: magnesium sulphate, ammonia alum, thorium, uranium and copper nitrates, and ferric chloride.

[Compare somewhat similar work on lactose, Trey, Abstr., 1904, i, 292.] J. C. P.

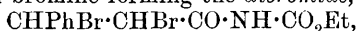
Cæsium Methylamide. ETIENNE RENGADE (*Compt. rend.*, 1905, 140, 246—248).—Moissan has shown that cæsium reacts with ammonia at 40° to form cæsium-ammonium (compare Abstr., 1903, ii, 477), and the author finds that, although the metal dissolves in methylamine at -20°, the solution of cæsium-methylammonium thus obtained decomposes readily, giving off hydrogen and forming cæsium-methylamide, NHMeCs, in white, silky crystals, which decompose explosively on being rapidly heated or on contact with moist air; at 115° to 120°, however, they are gradually decomposed with the formation of cæsium cyanide and the liberation of hydrogen, and they are slowly decomposed by water yielding methylamine and cæsium hydroxide. M. A. W.

Diaminoguanidine. GUIDO PELLIZZARI and C. CANTONI (*Ber.*, 1905, 38, 283—284).—A claim for priority (compare Stollé and Hofmann, this vol., i, 28). W. A. D.

Condensation of some Esters with Ethyl Carbamate and with Ethyl Aminoacetate. OTTO DIELS and HANS HEINTZEL (*Ber.*, 1905, 38, 297—305).—*Ethyl bromoacetylcarbamate*,
 $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$,

prepared by boiling an ethereal solution of ethyl bromoacetate and ethyl sodiocarbamate, $\text{CHNa}\cdot\text{CO}_2\text{Et}$, crystallises from dilute alcohol in long, slender needles and melts at $120\text{--}121^\circ$. *Ethyl α -bromopropionylcarbamate*, $\text{CHMeBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, prepared in similar manner from ethyl α -bromopropionate, crystallises from dilute alcohol or from ethyl acetate in short, thick prisms, sinters at 97° , and melts at $100\text{--}101^\circ$. *Ethyl α -bromobutyrylcarbamate* is similar and melts at $80\text{--}81^\circ$; *ethyl α -bromoisobutyrylcarbamate* melts at $63\text{--}64^\circ$. As the length of the carbon chain of the halogen acid increases, the ease of interaction with ethyl carbamate diminishes.

Ethyl cinnamoylcarbamate, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, prepared from ethyl cinnamate and ethyl carbamate, crystallises from a mixture of light petroleum and ethyl acetate in long needles, melts at $110\text{--}111^\circ$, and combines with bromine forming the *dibromide*,



which melts at $131\text{--}132^\circ$.

Ethyl sodiocarbamate simply eliminates 2HBr from two molecules of ethyl bromomalonate, giving rise to ethyl ethylenetetracarboxylate, $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{C}(\text{CO}_2\text{Et})_2$.

In presence of potassium hydroxide, ethyl aminoacetate combines with ethyl chloroacetate, alcohol being eliminated, to form *ethyl chloroacetylaminacetate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which crystallises from a mixture of ethyl acetate and light petroleum in thin, rectangular plates and melts at $62\text{--}63^\circ$. *Ethyl cyanoacetylaminacetate*, obtained in similar manner from ethyl cyanoacetate, crystallises from water and melts at $100\text{--}101^\circ$.

Ethyl aminoacetate combines with ethyl sodiocarbamate, alcohol being eliminated, to form ethyl hydantoate, which was not isolated, but characterised by its giving rise to hydantoin. W. A. D.

Internally Complex Metallic Salts. [Copper Glycine.] HEINRICH LEY (*Zeit. Elektrochem.*, 1904, 10, 954—956).—The molecular weight of copper glycine dissolved in water as determined by the freezing point method is almost normal, and its conductivity in aqueous solution is very small. It is therefore very little dissociated. The copper in this salt has been represented as replacing the hydrogen of the carboxyl groups or that of the amino-groups. The latter formula is doubtful, because diethylaminoacetic acid forms a salt which is quite analogous to the copper salt of glycine. The following experiments prove that the copper is linked to oxygen and not to nitrogen. When ammonia is added to a solution of copper glycine, no change in the deep blue colour of the solution takes place, but by determining the coefficient of partition of the ammonia between the solution and chloroform it is shown that the ammonia has combined with the salt. The combination might yield the salt $\text{Cu}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_4)_2$ or the complex cation $[\text{Cu}(\text{NH}_3)_n]$ and the anion $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2$. An experiment showed that the blue colour moves toward the cathode when the solution is electrolysed, proving that the copper exists in the cation. In order to explain the dark blue colour of the solutions, the author supposes that the salts are internally complex, the NH_2 groups playing

the same part as the NH_3 molecules attached to copper in the complex copper ammonia compounds. T. E.

Hydrolysis of Leucine Ethyl Ester by the Pancreatic Ferment. OTTO WARBURG (*Ber.*, 1905, **38**, 187—188. Compare E. Fischer and Bergell, *Abstr.*, 1903, i, 694; 1904, i, 867).—When the synthetical racemic ethyl ester of leucine is left in contact with water and crude pancreatin at the ordinary temperature, the *d*-ester is not hydrolysed, whereas the *l*-ester yields *l*-leucine. Fresh pancreas juice has the same effect. This affords a further example of "asymmetric hydrolysis." J. J. S.

Betaine Ethyl Ester Hydrochloride. ALBERT KOEPPEN (*Ber.* 1905, **38**, 167—169).—*Betaine ethyl ester hydrochloride*, prepared by the action of 33 per cent. alcoholic solution of trimethylamine on ethyl chloroacetate, separates from ethyl alcohol in deliquescent crystals and melts at 143.5° . Its *platinichloride*, $(\text{NMe}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et})_2\text{PtCl}_6$, forms glistening, orange-coloured crystals. When boiled for two hours with hydrochloric acid, betaine ethyl ester hydrochloride forms betaine hydrochloride, which was identified by its crystalline form and by its platinichloride.

Betaine ethyl ester itself could not be prepared by the action of moist silver oxide on its hydrochloride. A. McK.

Formation of C-Acyl Derivatives from Ethyl Cyanoacetate by means of Pyridine and Quinoline. ARTHUR MICHAEL and O. ECKSTEIN (*Ber.*, 1905, **38**, 50—53. Compare Dieckmann and Breest, *Abstr.*, 1904, i, 845).—The experiments of Claisen and Haase (*Abstr.*, 1900, i, 373) make it probable that the question whether an *O*- or a *C*-derivative is formed in the acylation of ethyl acetoacetate and similar compounds by the pyridine method depends on the stability of the primary additive product towards the base.

Ethyl cyanoacetoacetate, prepared by the action of acetyl chloride and pyridine on ethyl cyanoacetate in the cold, forms a *semicarbazone*, crystallising in colourless needles and melting at 190° .

When benzoyl chloride is added to a mixture of ethyl cyanoacetate and pyridine, even at a low temperature, a brown substance is produced. On replacing the pyridine by quinoline, however, ethyl cyanobenzoylacetate is obtained (compare Haller, *Abstr.*, 1886, 240). A neutral compound containing nitrogen, but of unknown constitution, was also obtained, crystallising from dilute alcohol in almost colourless microscopic needles, melting at 178° and dissolving readily in organic solvents.

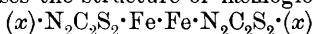
Ethyl ethylacetoacetate and ethyl methylacetoacetate do not yield acetyl derivatives with acetyl chloride and pyridine. C. H. D.

Supposed Existence of Thiocyanate of Iron and Probable Constitution of the Hæmoglobin of the Blood. NAZARENO TARUGI (*Gazzetta*, 1904, **34**, ii, 326—348. Compare *Abstr.*, 1903, ii, 460, and 1904, ii, 220; and Vitali, *Abstr.*, 1904, ii, 104 and 600).—Free thiocyanic acid does not give van Deen's reaction, because this is

characteristic of the normal thiocyanogen group, while the free acid contains the *iso*-form, which, when introduced into a salt, is converted wholly or partially into the thiocyanogen group. The red coloration formed by the action of ferric chloride on a thiocyanate is due to the formation of the iron salt of a *peroxythiocyanic acid* according to the reversible equation: $12\text{FeCl}_3 + 6\text{H}_2\text{O} + 6\text{KCNS} \rightleftharpoons 2\text{FeHC}_3\text{N}_3\text{O}_3\text{S}_3 + 6\text{KCl} + 10\text{FeCl}_2 + 10\text{HCl}$. The free acid, $\text{C}_3\text{H}_3\text{O}_3\text{N}_3\text{S}_3$, as well as all its acid salts, have a red colour. Solutions of oxalates, tartrates, &c., decolorise the acid and convert it into the corresponding normal salts, which are again decomposed by mineral acids with liberation of the peroxy-acid and formation of a red coloration. When a dilute solution of the free acid is heated, it becomes decolorised, and oxygen is liberated from the acid while the sulphur present is oxidised to sulphuric acid. With concentrated solutions, heating produces an increase in the depth of colour.

Peroxythiocyanic acid may also be prepared by the oxidation of thiocyanates in ethereal solution by means of nitric or chromic acid. The ethereal solution of the acid is decolorised by reducing agents.

The author expresses the structure of hæmoglobin as



and that of oxyhæmoglobin as $(x) \cdot \text{N}_2\text{C}_2\text{S}_2\text{O}_2 \cdot \text{Fe} \cdot \text{Fe} \cdot \text{N}_2\text{C}_2\text{S}_2\text{O}_2 \cdot (x)$, where (x) represents an albumin group. T. H. P.

Two Complex Salts of Molybdenum. ALBERTO CHILESOTTI (*Gazzetta*, 1904, 34, ii, 493—503).—The interaction of the double chloride of molybdenum and potassium (Abstr., 1903, ii, 730) with potassium thiocyanate yields a *thiocyanate of molybdenum and potassium*, $\text{K}_3\text{Mo}(\text{CNS})_6 \cdot 4\text{H}_2\text{O}$, which forms orange-coloured crystals readily soluble in water and readily loses water of crystallisation, becoming dark red, or, if completely dehydrated in a desiccator over phosphoric oxide or by heating, almost black in colour. In the neutral solution of the double salt, hydrogen peroxide produces a green coloration, which changes to blue and finally to yellow; hydrogen cyanide appears to be formed in this oxidation. Bromine added to an alkaline solution of the salt produces the same changes of colour. Lead acetate gives an orange-yellow precipitate insoluble in acetic acid, silver nitrate a flocculent yellow precipitate, and mercuric nitrate a brick-red precipitate, which becomes black on boiling the solution. Mercuric chloride yields a vivid red precipitate which turns yellow and has probably the composition $[\text{Mo}(\text{SCN})_6]_2\text{Hg}_2$.

With potassium cyanide, the double chloride of potassium and molybdenum yields the *double cyanide*, $\text{Mo}(\text{CN})_6\text{K}_4 \cdot 2\text{H}_2\text{O}$, which forms yellow crystals, readily soluble in water, yielding a neutral solution. The solution is stable when kept away from strong light, but when exposed to the direct action of the sun's rays, its colour changes almost instantaneously to red and then to pale green, hydrogen cyanide being simultaneously formed. That the formula of the salt is that given above, and not a multiple of it, is shown by conductivity determinations. Even in extremely dilute solution, ferric chloride is coloured an intense blue by solutions of the double cyanide. Solutions of silver and mercurous salts give voluminous, pale yellow precipitates

insoluble in dilute acids. This double cyanide presents the first known case of a complex ion which is stable in solution and which contains a metal combined with eight halogenic residues. T. H. P.

Condensation of Natural Leucine and Carbamic Acid.

LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1905, 140, 150—151).—iso *Butylhydantoic acid*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CH}_2\text{Pr}^\beta) \cdot \text{CO}_2\text{H}$, obtained by dissolving leucine in excess of carbamide at 130—135°, crystallises in very white needles decomposing at 200—210°, is slightly soluble in cold, readily so in boiling water or alcohol, insoluble in mineral acids, but dissolves in acetic acid, forms soluble salts with the alkali metals, and is decomposed by sodium hypobromite forming leucic acid. iso *Butylhydantoin*, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{CH}_2\text{Pr}^\beta \\ \text{NH} \cdot \text{CO} \end{array}$, obtained by heat-

ing *isobutylhydantoic acid* at 150°, crystallises in silky needles melting at 200—210°, is slightly soluble in cold water, readily soluble in cold alcohol, insoluble in mineral acids, but soluble in alkalis owing to the acid nature of the hydrogen atom of the imino-group situated between two carbonyls; it is not acted on by sodium hypobromite, and on prolonged boiling with water it is converted into *isobutylhydantoic acid*. M. A. W.

Cyanodialkylacetylcarbamides. FIRMA EMANUEL MERCK (D.R.-P. 156383. Compare this vol., ii, 179).—When the esters of dialkylcyanoacetic acids react with carbamide or its alkyl derivatives in the presence of a metallic ethoxide at the ordinary temperature, cyanodialkylacetylcarbamides are formed, which condense on heating to form iminodialkylbarbituric acids. Thiocarbamide or guanidine may also be employed in place of carbamide.

α-Cyano-α-ethylbutyrylcarbamide, $\text{CN} \cdot \text{CET}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, from ethyl *α-cyano-α-ethylbutyrate*, carbamide, and sodium ethoxide, crystallises from hot water, melts at 118°, and dissolves in alcohol, ether, or ethyl acetate. *Cyanoethylbutyrylthiocarbamide* forms slender, yellow needles and melts and decomposes at 261°. *Cyanoethylbutyrylguanidine* dissolves readily in water. *α-Cyano-α-propylvalerylcarbamide* crystallises from alcohol in colourless prisms and melts at 101°. *Cyanoethylbutyrylphenylcarbamide*, from ethyl cyanoethylbutyrate and phenylcarbamide, forms long, flat prisms and melts at 156°. C. H. D.

Preparation, Use, and Recovery of Semicarbazide. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1905, [iii], 33, 162—165).—Details are given of a method of preparing semicarbazide, which is a slight modification of that used by Thiele and Stange (*Abstr.*, 1894, i, 165). In the preparation of semicarbazones, the authors dissolve free semicarbazide in as little water as possible, add to the solution a few drops of acetic acid, and finally the aldehyde or ketone and sufficient methyl or ethyl alcohol to give a clear solution, which is finally warmed on the water-bath for 15 minutes. This process gives better results than the use of semicarbazide hydrochloride in combination with sodium acetate.

In regenerating a ketone or aldehyde from its semicarbazone, the latter is boiled for one hour in a reflux apparatus with a slight excess of dilute sulphuric acid (15 per cent.), and the aldehyde or ketone finally distilled off in a current of steam. The residue contains hydrazine sulphate and semicarbazide sulphate. On concentration and cooling, the former crystallises out from the mother liquor; after neutralisation with potassium carbonate and concentration under reduced pressure, two-thirds of the hydrazine initially used may be recovered as the sulphate by extraction with alcohol. T. A. H.

Imino-CC-dialkylbarbituric Acids. FIRMA EMANUEL MERCK (D.R.-P. 156384. Compare Abstr., 1903, i, 799; 1904, i, 389; this vol., i, 178).—Carbamide reacts with the esters of dialkylcyanoacetic acids on warming with sodium ethoxide in alcoholic solution on the water-bath, forming iminodialkylbarbituric acids, $\text{CRR}'\left\langle \begin{array}{c} \text{C}(\text{NH})\cdot\text{NH} \\ \text{CO} \text{---} \text{NH} \end{array} \right\rangle \text{CO}$, from which the corresponding dialkylbarbituric acids are readily obtained by heating with dilute acids.

Iminodiethylbarbituric acid, from carbamide and ethyl cyanoethylbutyrate, melts and decomposes at 195° and dissolves in 136 parts of water at 20° and in 23.5 parts at 100° . *Iminodipropylbarbituric acid* melts and decomposes at 305° ; *iminodibenzylbarbituric acid* crystallises from hot alcohol; *iminoethylpropylbarbituric acid* melts at 302° .

C. H. D.

Preparation of Barbituric Acid and its Homologues. FIRMA EMANUEL MERCK (D.R.-P. 156385. Compare preceding abstract).—Dilute acids hydrolyse the alkyl derivatives of iminobarbituric acid on heating, yielding alkylated barbituric acids.

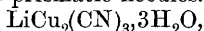
Dipropylbarbituric acid melts at 146° ; *dibenzylbarbituric acid* melts at 222° ; *propylbarbituric acid* (from *iminopropylbarbituric acid* melting at about 300°) melts at 207° ; *ethylpropylbarbituric acid* forms large, colourless needles and melts at 145° .

C. H. D.

Nitriles of Hydroxy- and Amino-carboxylic Acids. EMIL KNOEVENAGEL (*Ber.*, 1905, 38, 213—217. Compare *Trans.*, 1904, i, 981, 989, 994, 1024, 1027, 1028).—Polemical. A reply to Bucherer's criticisms (this vol., i, 59).

J. J. S.

Copper Double Cyanides. HERMANN GROSSMANN and PETER VON DER FORST (*Zeit. anorg. Chem.*, 1905, 43, 94—110. Compare Abstr., 1904, i, 983).—The sodium salt, $\text{NaCu}_2(\text{CN})_3\cdot 2\text{H}_2\text{O}$, prepared by the action of cuprous cyanide on a concentrated solution of sodium cyanide, forms glistening, monoclinic crystals. The ammonium salt, $\text{NH}_4\text{Cu}_2(\text{CN})_3\cdot \text{H}_2\text{O}$, forms prismatic needles. The lithium salt,

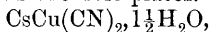


forms prismatic needles. These three salts are readily decomposed by water.

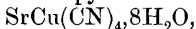
The rubidium salt, $\text{Rb}_2\text{Cu}_3(\text{CN})_5$, crystallises in octahedral leaflets. The caesium salt, $\text{Cs}_2\text{Cu}_3(\text{CN})_5$, separates in tetragonal or hexagonal

cubes. The *calcium* salt, $\text{CaCu}_3(\text{CN})_5$, forms rhombic, prismatic needles.

The *ammonium* salt, $\text{NH}_4\text{Cu}(\text{CN})_2$, prepared by careful evaporation at 70° of the liquid from which the salt $\text{NH}_4\text{Cu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ has been removed, separates in nacreous leaflets. The *rubidium* salt, $\text{RbCu}(\text{CN})_2$, prepared by the interaction of rubidium carbonate, cuprous cyanide, and hydrocyanic acid, forms rhombic plates. The *cæsium* salt,



forms glistening needles. The *barium* salt, $\text{BaCu}_2(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, crystallises in plates and in rhombic pyramids. The *strontium* salt,



forms monoclinic plates. The *magnesium* salt, $\text{MgCu}_2(\text{CN})_4 \cdot 11\text{H}_2\text{O}$, separates in monoclinic needles.

The *cæsium* salt, $\text{Cs}_2\text{Cu}(\text{CN})_3 \cdot \text{H}_2\text{O}$, crystallises in leaflets. The *barium* salt, $\text{BaCu}_2(\text{CN})_3 \cdot 3\text{H}_2\text{O}$, forms prismatic needles. The *calcium* salt, $\text{CaCu}(\text{CN})_3 \cdot 4\text{H}_2\text{O}$, forms prismatic needles. The authors have obtained these salts from mother liquors from which other salts had been removed.

From determinations of the lowering of freezing point, the conclusion is drawn that the salt $\text{K}_3\text{Cu}(\text{CN})_4$ undergoes hydrolytic dissociation in very dilute solution.

The *sodium* salt, $\text{Na}_3\text{Cu}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, forms hygroscopic, hexagonal leaflets. Its electrolytic conductivity was measured.

Crystallographic measurements of most of the salts examined are given. A. McK.

Derivatives of Formhydroxamic Acid and the Possible Existence of Esters of Fulminic Acid. HENRY C. BIDDLE (*Amer. Chem. J.*, 1905, **33**, 60—68).—Attempts have been made to prepare benzyl fulminate and the corresponding benzoyl and acetyl derivatives by the elimination of hydrogen chloride from the benzyl, benzoyl, and acetyl derivatives of chloro-formoxime (Abstr., 1900, i, 137), but without success.

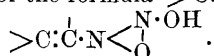
Methyl formhydroxamate, $\text{COH} \cdot \text{NH} \cdot \text{OMe}$, prepared by the action of formic acid on α -methylhydroxylamine, is a colourless liquid, which boils at 116 — 117° under 33 mm., at 123 — 124° under 45 mm., and at 126 — 127° under 50 mm. pressure; it solidifies in colourless prisms and melts at 38 — 39° . The ester is deliquescent and is decomposed by hydrochloric acid with formation of formic acid and α -methylhydroxylamine hydrochloride. When treated with solution of platinic chloride, the ester undergoes dissociation, and the platinichloride of α -methylhydroxylamine is produced. The *silver* salt of methyl formhydroxamate forms white leaflets and reacts with acetyl and benzoyl chlorides and with methyl and ethyl iodides with formation of the corresponding acyl and alkyl derivatives. When molecular proportions of methyl formhydroxamate and phenylcarbimide are warmed together, an additive *compound* is produced, which crystallises in colourless leaflets, melts at 123 — 123.5° , and is readily soluble in chloroform and sparingly so in ether, alcohol, or hot water.

By the action of phosphorus pentachloride on methyl formhydroxamate, *methyl chloroformoxime*, $\text{CHCl} \cdot \text{N} \cdot \text{OMe}$, is produced as a

volatile liquid, which boils at 68° , has an odour like that of chloroform, and is slightly soluble in water. When this substance is treated with potassium hydroxide, small quantities of a neutral unsaturated compound are produced, which has a strong odour resembling that of isonitriles, boils at about $50-60^{\circ}$, and is probably methyl fulminate, $C:N\cdot OMe$, but has not yet been isolated in sufficient quantity to admit of its identification. Methyl fulminate also appears to be formed by the interaction of α -methylhydroxylamine hydrochloride, chloroform, and alcoholic potassium hydroxide, the same isonitrile-like odour being produced. E. G.

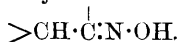
Nitrimines and Nitriminic Acids. ROLAND SCHOLL (*Annalen*, 1905, 338, 1—35).—The ketoximes of the fatty series are converted by nitrous acid or nitrogen peroxide into ψ -nitroles, but in the case of the oximes of pinacolin, camphor, camphenone, fenchone, menthone, tanacetone, mesityl oxide, and santonin, the oxime group is exchanged for the group N_2O_2 . This reaction is confined to ketoximes in which the group $>C:N\cdot OH$ is linked to a tertiary or quaternary carbon atom. The group, $C_2HN_2O_2$, which is produced in this reaction must either have the constitution $>C:\overset{|}{C}\cdot NH\cdot NO_2$, an enylnitroamine, or $>CH:\overset{|}{C}\cdot N\cdot NO_2$, a nitroimine. Since the compounds do not react with phenylcarbimide and diazomethane, the latter formula is the more probable.

The nitroimines are ψ -acids and yield a series of salts which correspond with an acid of the formula $>C:\overset{|}{C}\cdot N:NO\cdot OH$ or



When the acid is set free from its salts, it is immediately reconverted into the nitroimine, but, since the salts yield the two series of alkyl derivatives, $>C:\overset{|}{C}\cdot N\begin{array}{c} \nearrow N\cdot OR \\ \searrow O \end{array}$ and $>C:\overset{|}{C}\cdot NR\cdot NO_2$, it is probable that an enylnitroamine is intermediately produced in the conversion.

Of the two possible constitutions of the group present in the salts $N_2O\cdot OH$, the expression, $N\begin{array}{c} \nearrow N\cdot OH \\ \searrow O \end{array}$, is preferred, since it represents more simply the cleavage of the mesitylnitroiminic acid into nitrous acid and α -mesityloxime, and at the same time the formation of nitroimines from oximes and nitrous acid. Only those oximes are capable of undergoing this reaction which have a loosely bound hydrogen atom on the β -carbon atom relatively to the oxime group, thus:



This hydrogen atom, together with the hydrogen atom of the oxime group, combines with the oxygen of the nitrous acid in the condensation; a group $\begin{array}{c} >C \\ | \\ -C:N\cdot O \end{array} \nearrow N\cdot OH$ is thus formed, which then, by re-

arrangement, passes into the group $>C:\overset{|}{C}\cdot N\begin{array}{c} \nearrow N\cdot OH \\ \searrow O \end{array}$.

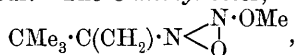
[With A. O. WEIL and K. HOLDERMANN.]—Pinacolinoxime on
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treatment with phosphorus pentachloride in dry ether is converted into *acetyl-tert.-butylamide*, $\text{CMe}_3 \cdot \text{NHAc}$, which crystallises in needles, melts at 95° , sublimes very readily and boils at 194° ; its *hydrochloride* formed from the ethereal solution is very hygroscopic. From this transformation, it follows that the oxime has the anti-configuration, $\text{Me} \cdot \text{C} \begin{smallmatrix} \text{C} \cdot \text{CMe}_3 \\ \text{N} \cdot \text{OH} \end{smallmatrix}$. Pinacolinoxime reacts with phenylcarbamide, yielding

the compound $\text{C}_6\text{H}_{12} \cdot \text{NO} \cdot \text{CO} \cdot \text{NHPh}$, which crystallises in needles melting at 131.5° . The *acetyl* derivative of the oxime, $\text{C}_6\text{H}_{12} \cdot \text{N} \cdot \text{OAc}$, is an oil boiling at $83-84^\circ$ under 10 mm., at $100-101^\circ$ under 25 mm., and at $208-216^\circ$ under the atmospheric pressure.

Pinacolin-nitroimine, $\text{CMe}_3 \cdot \text{CMe} \cdot \text{N} \cdot \text{NO}_2$, is prepared by dissolving pinacolinoxime in ether and adding nitrogen peroxide, and by fractionating the product after removal of the acid by water and alkali. It boils at $80.5-81^\circ$, and is always mixed with oxime and methyl-*tert.*-butyldinitromethane, $\text{CMe}_3 \cdot \text{CMe}(\text{NO}_2)_2$, which separates as a crystalline hydrochloride when the nitroimine is dissolved in concentrated hydrochloric acid; it forms very volatile crystals smelling of camphor, melts at $173-174^\circ$, and boils at $101-103^\circ$ under 34 mm. pressure. The salts of the nitroimine are formed when it is heated with concentrated alkali hydroxides, but the ammonium salt is not produced by passing dry ammonia into a solution in anhydrous ether. It is oxidised by permanganate and reduces ammoniacal silver solutions. It does not react with diazomethane or phenylcarbimide, and, when distilled under the ordinary pressure, decomposes into pinacolin. On bromination, it yields dibromopinacolin, $\text{C}_6\text{H}_{10}\text{OBr}_2$ (m. p. 74.5°), which is identical with the substance obtained from $\delta\delta$ -dibromo- $\beta\beta$ -dimethyl- γ -butanone. On reduction with aluminium amalgam in moist ether, the nitroimine is converted into the oxime.

The *sodium* salt, obtained from the nitroimine by the use of sodium ethoxide, crystallises in silky, hygroscopic needles, which are hydrolysed in aqueous solution; the *potassium* salt forms hygroscopic needles, and the *silver* salt, a greyish-white precipitate. When the sodium salt is heated in methyl-alcoholic solution with methyl iodide for 2 hours, a *N-methyl* derivative, $\text{CMe}_3 \cdot \text{C}(\text{CH}_2) \cdot \text{NMe} \cdot \text{NO}_2$, is obtained in the form of volatile crystals melting at 39° and decomposed by hydrochloric acid, methylamine being produced; it is not oxidised by permanganate. The corresponding *ethyl*, *isopropyl* and *n-butyl* derivatives, are oily liquids of peculiar odour. The *O-methyl* ester,

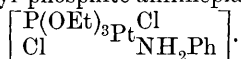


is prepared from the silver salt and methyl iodide at a low temperature in ethereal solution; it is an oil which is readily oxidised by alkaline permanganate and decomposed by hydriodic acid, methyl iodide being formed. The corresponding ethyl ester is a yellow oil. The nitroimine also yields a series of *N*-acyl derivatives when the sodium salt is treated with acyl chlorides in hot anhydrous alcohol; the *acetyl*, *benzoyl*, and *benzenesulphonic* compounds were all thus prepared, and formed oils which are not decomposed by water.

K. J. P. O.

Platinum Phosphorus Halogen Compounds and their Derivatives. II. ARTHUR ROSENHEIM and WALTER LEVY (*Zeit. anorg. Chem.*, 1905, 43, 34—47. Compare Abstr., 1904, ii, 131).—By the action of organic amines on alkyl phosphite-platochlorides, two series of isomeric compounds, $\text{RNH}_2\text{PtCl}_2\text{P(OR')}_3$, are produced. The stable series probably corresponds with platosoammine chloride and the labile with platosemidiammine chloride.

When aniline is gradually added to a solution of ethyl phosphite-platochloride, $[\text{P(OEt)}_3\text{PtCl}_2]_2$, in alcohol or benzene at 0° , crystals of the *yellow* compound, $\text{PtPCl}_2\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}$, first separate, whilst from the filtrate silky needles of a colourless *compound*, isomeric with the former, separate. The relative proportion of those compounds produced is dependent on the temperature conditions, the latter being formed in larger amount the higher the temperature. The yellow compound is the labile form; at its melting point, 108° , it is transformed into the white variety, which melts at 147° . The transformation is also effected on exposure at the ordinary temperature or on rubbing with a glass rod. The yellow form is probably *cis*-triethyl phosphite-anilineplatochloride, $\left[\begin{smallmatrix} \text{Cl} & \text{P(OEt)}_3 \\ & \text{Pt} \\ \text{Cl} & \text{NH}_2\text{Ph} \end{smallmatrix} \right]$, whilst the white compound is probably *trans*-triethyl phosphite-anilineplatochloride,



The analogous *pyridine* compounds, $\text{PtPCl}_2\text{C}_{11}\text{H}_{20}\text{O}_3\text{N}$, were prepared. The two isomerides were crystalline and resembled the corresponding aniline compounds.

The action of ammonia was different from that of the organic bases. When a current of dry ammonia was passed into a solution of triethyl phosphite-platochloride in benzene, voluminous white crystals of the *compound* $[\text{Pt(NH}_3)_2\text{P(OEt)}_3]_2\text{Cl}_4$ separated. It is a good electrolyte as distinct from the compounds with aniline and pyridine described. With chloroplatinic acid, it forms the *platinichloride*, $[\text{Pt(NH}_3)_2\text{P(OEt)}_3]\text{PtCl}_6$.

The action of ammonia on methyl diphosphite-platochloride is analogous, white crystals of the *compound* $[\text{Pt(NH}_3)_2(\text{P[OMe]}_3)_2]\text{Cl}_2$, being produced.

Phenyl diphosphite-platochloride, $[\text{PtCl}_2(\text{P[OPh]}_3)_2]$, separates from alcohol in white crystals and melts at 155° .

The platinum phosphorus bromo-compounds described behave similarly to the corresponding chloro-compounds.

Phosphorus bromide-platobromide, $[\text{PtBr}_2(\text{PBr}_3)]_2$, prepared by the action of phosphorus pentabromide on platinum black, forms reddish-brown crystals which, by an excess of phosphorus tribromide, are converted into *diphosphorus bromide-platobromide*, $[\text{PtBr}_2(\text{PBr}_3)_2]$, which is readily acted on by moisture and reacts violently with methyl alcohol to form the *ester*, $[\text{PtBr}_2(\text{P[OMe]}_3)_2]$, which melts at 136° . When ethyl alcohol is used instead of methyl alcohol in the latter reaction, the reaction proceeds normally, triethyl phosphite-platobromide, $[\text{P(OEt)}_3\text{PtBr}_2]_2$, being produced. By the action of aniline on the latter compound, two isomerides are formed, as in the case of the action on the corresponding chloro-compound.

The *compound* $[\text{PtBr}_4(\text{OP[OEt]}_3)_2]$ melts at 155° .

A. McK.

Primary Arsines. WILLIAM M. DEHN (*Amer. Chem. J.*, 1905, 33, 101—153. Compare Palmer and Dehn, *Abstr.*, 1902, i, 86).—Primary arsines can be readily prepared by the reduction of alkylarsonic acids with amalgamated zinc dust and hydrochloric acid.

A detailed account is given of the method of preparation of methylarsine. Methylarsine is soluble in water to the extent of 85 parts per million. On oxidation with nitric acid, it is converted into arsenic oxide and methylarsonic acid. When the compound is passed into a neutral or alkaline solution of silver nitrate, silver is precipitated and methylarsonic acid is produced. If the gas is led into a solution of bromine in carbon disulphide, arsenic tribromide is formed. The arsine reacts with solution of iodine with formation of methylarsonic and hydriodic acids, $\text{AsH}_2\text{Me} + 6\text{I} + 3\text{H}_2\text{O} = \text{AsMeO}(\text{OH})_2 + 6\text{HI}$. When methylarsine is treated with dry hydrogen chloride or hydrogen sulphide, little or no action takes place. The compound is not affected by yellow phosphorus either at the ordinary temperature or at 100° . It is decomposed by aqueous mercuric chloride with formation of mercurous chloride and mercury methylarsonate. When methylarsine is heated with excess of methyl iodide for 8 hours in a sealed tube at 110° , tetramethylarsonium iodide is produced; with ethyl iodide, under similar conditions, methyltriethylarsonium iodide is formed.

Magnesium ethylarsonate, MgAsEtO_3 , may be prepared in the following manner. A solution of potassium arsenite is treated with ethyl iodide, and when the reaction is complete the solution is acidified with dilute hydrochloric acid and filtered. Chlorine is passed into the filtrate, the iodine is removed by filtration, the solution is rendered alkaline with ammonia, treated with a large excess of magnesia mixture, and left for 24 hours. The liquid is filtered, and, on evaporation, magnesium ethylarsonate separates. When dried at 140° , magnesium methylarsonate is obtained as a white powder, readily soluble in acids but insoluble in alkalis. It is soluble in water at 22° to the extent of 2.31 parts per 1000, and in 10 per cent. solution of ammonium chloride to the extent of 2.66 parts per 1000. At 25° , 0.125 gram dissolves in 1 litre of alcohol. The salt usually contains $1\text{H}_2\text{O}$, which is not completely removed at 145° . When hydrogen sulphide is passed into a solution of magnesium ethylarsonate in hydrochloric acid, *ethylarsine disulphide*, AsEtS_2 , is obtained as a viscid, yellow oil having a peculiar, disagreeable odour; it has a sp. gr. 1.836 at 24° , is easily soluble in benzene, chloroform, or carbon disulphide, and insoluble in water, alcohol, or ether, and is dissolved by dilute nitric acid with formation of ethylarsonic acid.

Trimethylarsine sulphide, Me_3AsS , obtained by the action of heat on methylarsine disulphide, crystallises in white, tough, lustrous needles and melts at 174° . Triethylarsine sulphide melts at 119.5° and reacts with hydrobromic acid with formation of triethylarsine dibromide and hydrogen sulphide.

Magnesium methylarsonate forms small, white crystals and is soluble in water to the extent of 2.118 grams per litre at 22° and 3.085 grams at 99° .

Silver phenylarsonate, $\text{Ag}_2\text{PhAsO}_3$, is obtained as a white, glistening

precipitate when silver nitrate is added to an ammoniacal solution of phenylarsonic acid; it is practically insoluble in water.

A series of experiments was carried out with the object of ascertaining the best conditions for the preparation of alkylarsonic acids by G. Meyer's reaction (Abstr., 1883, 1078). The results showed that a better yield is obtained with potassium arsenite than with the sodium salt, that ethyl iodide gives a better result than the bromide, and that in the aliphatic series the yields are inversely as the molecular weight of the alkyl haloid employed.

Ethylarsine, AsH_2Et , is a liquid which resembles methylarsine, boils at 36° , has a sp. gr. 1.217 at 22° , is soluble in water to the extent of 126 parts per million at 19° , and has an extremely disagreeable, penetrating odour. It combines with oxygen with formation of ethylarsine oxide and water, is oxidised by concentrated nitric acid to ethylarsonic acid, arsenic oxide, and acetic acid, and when passed into silver nitrate solution is converted into ethylarsonic acid, silver being precipitated. When the arsine is led into concentrated sulphuric acid, white crystals are obtained which probably consist of the salt, $2\text{AsH}_2\text{Et}, \text{H}_2\text{SO}_4$. By the action of ethyl iodide on ethylarsine at 110° , tetraethylarsonium iodide is produced. *Trimethylethylarsonium iodide* forms hard, glistening needles, softens at about 300° , and shrinks at 320° , and is soluble in water, chloroform, or hot alcohol. *Ethyltriisomylarsonium iodide* forms compact crystals, does not melt below 250° , is soluble in alcohol, and sparingly so in chloroform. When ethylarsine is heated with carbon disulphide for 10 hours in a sealed tube at 120° , triethylarsine sulphide is produced, together with small quantities of an oil with an irritating odour resembling that of cacodyl.

Phenylarsine boils at 93° under 70 mm., 84° under 50 mm., and at 77° under 33 mm. pressure, and is soluble in alcohol, ether, or carbon disulphide, but insoluble in water. When it is treated with bromine, a brick-red precipitate is produced which probably consists of the substance $\text{AsHPhBr}, \text{HBr}$; on exposure to the air, it becomes liquid and evolves hydrogen bromide, and by the action of zinc and hydrochloric acid is converted into phenylarsine. Phenylarsine decolorises solution of iodine with formation of phenylarsonic acid and other products. When the arsine is heated with excess of ethyl iodide for 6 hours at 120° , phenyltriethylarsonium iodide is produced. Phenyltrimethylarsonium iodide can be prepared in a similar manner. *Phenyltriisomylarsonium iodide* forms pearly-white crystals, melts at 163° , and is very soluble in chloroform or alcohol, but insoluble in benzene or cold water. When phenylarsine was heated with phenyl iodide, no arsonium iodide could be obtained. E. G.

Spatial Formula for Benzene. BERTHOLD KÖNIG (*Chem. Zeit.*, 1905, 29, 30).—The author suggests a "cube" formula for benzene, in which the six carbon atoms are arranged in six of the corners of a cube in such a manner that each carbon atom is united by one bond to one hydrogen atom, by two bonds, one to each of the two neighbouring carbon atoms, whilst the fourth bond extends to one of the two remaining corners of the cube which are not occupied by carbon atoms. The three bonds which extend to each of those two corners are supposed to mutually satisfy one another.

In substitution compounds of benzene, this formula is transformed into a plane hexagonal type. A. McK.

Hydrolysis of Methyl Benzenesulphonate. ARTHUR PRAETORIUS (*Monatsh.*, 1905, **26**, 1—34. Compare Wegscheider, *Abstr.*, 1902, ii, 493; Wegscheider and Furcht, *Abstr.*, 1903, i, 342).—The hydrolysis of methyl benzenesulphonate with water is a unimolecular reaction, and the rate of hydrolysis, therefore, is proportional to the concentration of the ester. As the hydrolysis constant with 0.05375 *N*-sulphuric acid, *K* 0.0007175, is little greater than that with water, *K* 0.0007015, the hydrolysis in aqueous solution cannot be accelerated by the presence of hydrogen ions. The formula for the alkaline hydrolysis of carboxylic esters is not applicable to sulphonic esters, as in the hydrolysis of methyl benzenesulphonate with an alkali the action of the water cannot be neglected; it must be replaced by Wegscheider's formula (*loc. cit.*). G. Y.

Triphenylmethyl. PAUL JACOBSON (*Ber.*, 1905, **38**, 196—199. Compare Tschitschibabin. This vol., i, 125).—The author agrees with Tschitschibabin that Ullmann and Borsum's hexaphenylethane is most probably benzhydryltetraphenylmethane, but is of opinion that Gomberg's triphenylmethyl should not be represented as hexaphenylethane, but rather as 4-triphenylmethyl-1-diphenylmethylene-cyclo- $\Delta^{2,5}$ -hexadiene, $\text{CPh}_2\text{:C} \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{CH} \cdot \text{CPh}_3$.

Such a formula accounts for the bimolecular nature of triphenylmethyl and at the same time, by a rupture at the dotted line, indicates how the compound could readily react as free triphenylmethyl.

It also accounts for the transformation of Gomberg's compound into Ullmann and Borsum's so-called hexaphenylethane by the wandering of a single hydrogen atom. J. J. S.

Condensation of Benzaldehyde with Toluene. ALFRED KLIEGL (*Ber.*, 1905, **38**, 84—87).—Griepentrog found (*Abstr.*, 1886, 887) that benzaldehyde and toluene condense together in the presence of zinc chloride, but was unable to obtain a crystalline product. Benzaldehyde does not condense with benzene in presence of concentrated sulphuric acid, but toluene condenses slowly in the cold. After removal of unaltered benzaldehyde and toluene, the product is extracted with ether and finally distilled by means of superheated steam. *Phenyldi-p-tolylmethane* crystallises from methyl alcohol and melts at 54—54.5°. Crystallisation only takes place slowly, as the compound tends to separate in an oily state, and inoculation with a crystal is necessary.

Phenyldi-p-tolylcarbinol, prepared by the addition of methyl benzoate and magnesium to an ethereal solution of *p*-bromotoluene, separates on cooling its solution in light petroleum in a freezing mixture in large, colourless crystals, sintering at 75° and melting at 76.5—77.5°. Its solution in glacial acetic acid gives a yellowish-green coloration with concentrated sulphuric acid. Zinc dust and acetic acid reduce it to phenyldi-*p*-tolylmethane, identical with that just described.

C. H. D.

Phenylfluorene. ALFRED KLIEGL (*Ber.*, 1905, 38, 284—297).—

Phenylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CHPh}$, is best prepared by distilling triphenylcarbinol with crystalline phosphoric acid. Phenylfluorenol, obtained by Ullmann and von Wurstemberger's method (*Abstr.*, 1904, i, 154), crystallises from carbon tetrachloride with $\frac{1}{2}\text{CCl}_4$, and melts, when free from solvent, at $107\text{--}107.5^\circ$. Bromine at the ordinary temperature (1 mol.) converts phenylfluorene dissolved in carbon disulphide into

9-bromo-9-phenylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CBrPh}$, which crystallises from light

petroleum in slender needles and melts at 99° ; on treating the bromo-compound with hot methyl alcohol, the *methyl* ether, $\text{C}_{19}\text{H}_{13}\cdot\text{OMe}$, is obtained in long prisms melting at $92.5\text{--}93^\circ$; the *ethyl* ether, $\text{C}_{19}\text{H}_{13}\cdot\text{OEt}$, obtained in similar manner, crystallises in small prisms and melts at 113° . Bromophenylfluorene is very stable towards boiling water and alkalis, but is converted into phenylfluorenol by heating with hydrated sodium acetate in glacial acetic acid solution. The *acetyl* derivative of phenylfluorenol separates from acetic acid or alcohol in prismatic crystals and melts at $169\text{--}169.5^\circ$. Hydroxy-

diphenylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, prepared by condensing phenylfluorenol with phenol, crystallises from 96 per cent. alcohol in needles containing alcohol, or from acetic acid, and melts at $189.5\text{--}190^\circ$; the *acetyl* derivative, $\text{C}_{19}\text{H}_{13}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$, crystallises from acetic acid or alcohol in slender needles and melts at 176° . *Diphenylfluorene ether*, $\text{C}_{38}\text{H}_{26}\text{O}$, prepared by adding concentrated sulphuric acid to phenylfluorenol dissolved in glacial acetic acid, is sparingly soluble in all solvents save chloroform and decomposes between 320 and 360° .

9-Chloro-9-phenylfluorene, $\text{C}_{19}\text{H}_{13}\text{Cl}$, prepared by the action of phosphorus pentachloride on phenylfluorenol in benzene solution, crystallises from light petroleum, melts at $78\text{--}79^\circ$, and with aniline gives *anilino-*

phenylfluorene, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh}\cdot\text{NHPh}$, crystallising from light petroleum or alcohol and melting at 175° .

Phenylbenzylfluorene, $\text{C}_{26}\text{H}_{20}$, prepared by heating phenylfluorene with benzyl chloride and solid potassium hydroxide for 6 hours at 230° , crystallises from a mixture of glacial acetic acid and light petroleum and melts at $136\text{--}137^\circ$.

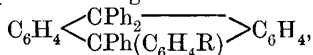
On nitration in cold glacial acetic acid solution, phenylfluorene gives rise to 2-nitro-9-phenylfluorene, $\begin{smallmatrix} \text{NO}_2\cdot\text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CHPh}$, which crystallises

from glacial acetic acid in leaflets and melts at 135° ; when the hydrocarbon is added to an excess of nitric acid of sp. gr. 1.52, *tetranitrophenylfluorene*, is obtained, which melts and decomposes at about 235° . 2-Nitro-9-phenylfluorene, on oxidation with chromic acid in acetic acid solution, gives 4-nitro-2-benzoylbenzoic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{COPh}$, which crystallises from benzene or water, melts at $161.5\text{--}162^\circ$, and gives a *methyl* ester crystallising in prisms and melting at 104.5° . 2-Nitro-anthraquinone, formed on heating 4-nitro-2-benzoylbenzoic acid with concentrated sulphuric acid at 100° , crystallises from light petroleum

in mossy aggregates of needles, melts at 180.5—181°, and is easily reduced by alkaline stannous chloride solution to 2-aminoanthraquinone. 4-Amino-2-benzoylbenzoic acid, prepared by the reduction of the corresponding nitro-compound with ammoniacal ferrous hydroxide, crystallises from alcohol in golden-yellow, efflorescent prisms with 1EtOH, and melts at 195°; 4-hydroxy-2-benzoylbenzoic acid, prepared by means of the diazo-reaction, decomposes at about 220—222° and is resolved by fusion with sodium hydroxide into benzoic and *p*-hydroxybenzoic acids.

W. A. D.

Syntheses in the Anthracene Series. III. 9:9:10:10-Tetraphenyldihydroanthracene and its Derivatives. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1905, 140, 283—287. Compare Abstr., 1904, i, 660).—When 9-hydroxy-9:10:10-triphenyldihydroanthracene is heated in glacial acetic acid solution with phenol, aniline, dimethyl- or diethyl-aniline, condensation takes place and mono-substituted derivatives of 9:9:10:10-tetraphenyldihydroanthracene are formed in almost quantitative yield. When phenol is employed, the addition of a small quantity of sulphuric acid is necessary for the reaction to take place. The general formula of the products is



where R represents either, OH, NH₂, NMe₂, or NEt₂.

The *hydroxy*-derivative crystallises in small prisms melting at about 308°. It is insoluble in alkalis, but dissolves very readily in alcoholic potash.

The *amino*-derivative forms small, white crystals melting at 320°. When diazotised and treated with β -naphthol, a red colouring matter is obtained. When the diazo-compound is boiled with absolute alcohol, there is no formation of hydrocarbon, but the *ethoxy*-derivative is obtained in small, white crystals melting at 265°. These crystals are only slightly soluble in the ordinary solvents. The *dimethylamino*-derivative forms small, white crystals melting at 285°. The *diethylamino*-derivative forms colourless needles melting at 216°.

9:10-Dihydroxy-9:10-diphenyldihydroanthracene condenses in a similar manner with dimethyl- and diethyl-anilines.

In each case, equal quantities of two isomerides are obtained, which can be very easily separated by reason of their great difference in solubility. They are evidently the *cis*- and *trans*-forms corresponding with



H. M. D.

9:10-Diphenylphenanthrene. HEINRICH BILTZ (*Ber.*, 1905, 38, 203—206. Compare Abstr., 1893, i, 718; 1897, i, 533).—The compound melting at 235° (corr.) which was previously obtained by

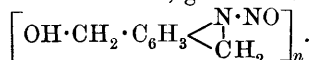
condensing benzene and chloral in the presence of aluminium chloride is identical with Werner and Grob's 9:10-diphenylphenanthrene (Abstr., 1904, i, 864). The same compound is obtained by the action of aluminium chloride on a benzene solution of tetraphenylethylene. The reaction is thus similar to the formation of phenylfluorene from triphenylmethane.

J. J. S.

Action of Ammonium Nitrite and Ammonium Nitrate (or of Nascent Nitrogen and Nitrous Oxide) on Aromatic Compounds. WILHELM VAUBEL (*Chem. Zeit.*, 1904, 28, 1245—1246).—The action of ammonium nitrite on aniline, *m*-phenylenediamine, sodium aminonaphthalenesulphonate, dimethylaniline, phenol, and benzaldehyde respectively, and of ammonium nitrate on naphthalene, anthracene, phenol, resorcinol, aniline, *o*-toluidine, *p*-toluidine, benzidine, *m*-phenylenediamine, *p*-phenylenediamine, diphenylamine, dimethylaniline, α - and β -ethylnaphthylamines, benzaldehyde, and benzoic acid respectively was examined. By the action of ammonium nitrite in aqueous solution at 60—70° on phenols, nitroso-compounds or their decomposition products are formed. By the action of ammonium nitrite on amines, diazo-compounds or their decomposition products are formed. Ammonium nitrate had often an oxidising action in the cases examined; aniline and other amines were oxidised. In other cases, by the action of ammonium nitrate, nitrogen was introduced into certain of the compounds investigated, as, for example, with phenol, naphthalene, benzaldehyde, and benzoic acid, oxidation proceeding at the same time.

A. McK.

Introduction of the Groups $\cdot\text{CH}_2\cdot\text{OH}$ and $\cdot\text{CH}_2\cdot$ into Primary Aromatic Amines and Preparation of Compounds of an Imidic Character. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1303—1311).—The action of formaldehyde solution on the sodium derivative of formanilide yields a yellow oil, $\text{C}_6\text{H}_4\left\langle \begin{smallmatrix} \text{N}\cdot\text{CH}_2\cdot\text{OH} \\ \text{CH}_2 \end{smallmatrix} \right\rangle$, which decomposes on distillation. When treated with dilute hydrochloric, nitric, or sulphuric acid, the oil congeals to an orange-coloured base having the composition $\left[\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\left\langle \begin{smallmatrix} \text{NH} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \right]_n$, which is soluble in acids, has a high molecular weight and, when treated with sodium nitrite in acid solution, gives a nitroso-compound,



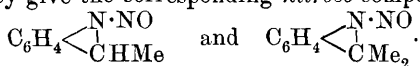
When boiled with an alkaline solution of β -naphthol, this nitrosocompound is converted into a red *azo-dye*, $\text{ONa}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{CH}_2\cdot\text{OH})_2$. With mercuric iodide dissolved in potassium iodide, mercuric cyanide dissolved in potassium or ammonium cyanide, or mercuric chloride, an acid solution of the base yields a yellow, powdery precipitate, which in the last case has the composition $\text{O}\left(\text{CH}_2\cdot\text{C}_6\text{H}_3\left\langle \begin{smallmatrix} \text{NH} \\ \text{CH}_2 \end{smallmatrix} \right\rangle\right)_2\cdot\text{HgCl}_2$. The precipitate obtained with gold chloride has the formula $\text{C}_7\text{H}_7\cdot\text{NAu}$.

The action of formaldehyde on the sodium derivative of formyl- β -

naphthylamine yields an *oil*, $C_{10}H_6 \begin{smallmatrix} & CH_2 \\ & | \\ < & N \cdot CH_2 \cdot OH \end{smallmatrix}$, which is converted by hydrochloric acid into an orange-coloured, pasty mass, precipitable from concentrated hydrochloric acid by water as a yellow *powder* having the composition $OH \cdot CH_2 \cdot C_{10}H_5 \begin{smallmatrix} & NH \\ & | \\ < & CH_2 \end{smallmatrix}$. With sodium nitrite, an acid solution of this base yields a slightly soluble *nitroso*-compound, $OH \cdot CH_2 \cdot C_{10}H_5 \begin{smallmatrix} & N \cdot NO \\ & | \\ < & CH_2 \end{smallmatrix}$, which gives a red *pigment* with alkaline β -naphthol solution. With mercuric salts, the base yields insoluble, yellow compounds, whilst aqueous ferric chloride oxidises the base in acid solution to a brown powder. Auric chloride precipitates a yellow powder which becomes brown on heating.

The action of formaldehyde solution on the sodium derivative of the anilide of sulphanilic acid yields the *base* $SO_3H \cdot C_6H_3 \begin{smallmatrix} & NH \\ & | \\ < & CH_2 \end{smallmatrix}$.

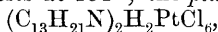
The sodium derivative of formanilide reacts also with acetaldehyde giving the *imine base*, $C_6H_4 \begin{smallmatrix} & NH(1) \\ & | \\ < & CHMe(4) \end{smallmatrix}$, and with acetone giving the *base*, $C_6H_4 \begin{smallmatrix} & NH(1) \\ & | \\ < & CMe_2(4) \end{smallmatrix}$. Like other iminic bases these give yellow precipitates with mercuric chloride, mercuric iodide in potassium iodide solution, platonic chloride, or auric chloride. With nitrous acid, they give the corresponding *nitroso*-compounds,



T. H. P.

Replacement of the Aldehyde Oxygen Atom by Two Univalent Hydrocarbon Radicles by means of Grignard's Reaction. FRANZ SACHS and LUDWIG SACHS (*Ber.*, 1905, **38**, 517—526).—*p*-isoPropyldimethylaniline, $NMe_2 \cdot C_6H_4Pr^{\beta}$, is formed when *p*-dimethylaminophenylmethylcarbinol is heated with an excess of magnesium methyl iodide at 100° , or when 1 mol. of *p*-dimethylaminobenzaldehyde is added to magnesium and methyl bromide, corresponding with at least 2 mols. of magnesium methyl bromide in absolute ethereal solution, the ether distilled off, and the residue heated at 100° for 6—8 hours. It is a colourless oil with an aromatic odour, boils at 235.6° (corr.) under 752 mm. pressure, is volatile in a current of steam, and has a sp. gr. 0.92286 at $18^\circ/18^\circ$ and n_D 1.5353 at 18° . The *methiodide*, $C_{12}H_{20}NI$, crystallises in glistening leaflets, melts at 198° (corr.), and, when treated with silver oxide in boiling aqueous solution, yields the strongly alkaline ammonium base, which crystallises in yellow leaflets and melts at $93-94^\circ$; the *ethobromide* crystallises in broad rose-coloured leaflets and melts at $66-67^\circ$; the *hydrochloride*, $C_{11}H_{17}N \cdot HCl$, crystallises in broad, glistening leaflets and melts at 155° ; the *platinichloride*, $(C_{11}H_{17}N)_2 \cdot H_2PtCl_6$, crystallises in large, golden-brown needles, blackens at about 197° , and melts and decomposes at $207-208^\circ$ (corr.); the *aurichloride* crystallises in long, lemon-yellow needles or broad leaflets and melts at 95° .

4-Dimethylamino-1- α -ethylpropylbenzene, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHEt}_2$, formed in the same manner from *p*-dimethylaminobenzaldehyde and magnesium ethyl bromide, is a yellow oil which boils at $127\text{--}129^\circ$ under 7 mm., at $262\cdot2^\circ$ (corr.) under 754 mm. pressure, is volatile in a current of steam, and has a sp. gr. $0\cdot91425$ at $19^\circ/19^\circ$ and n_D $1\cdot5266$ at 19° . The *methiodide*, $\text{C}_{14}\text{H}_{24}\text{NI}$, crystallises in large, silky leaflets and melts at $168\text{--}169^\circ$; the *hydrochloride*, $\text{C}_{13}\text{H}_{21}\text{N} \cdot \text{HCl}$ crystallises in large, glistening leaflets and melts at 131° ; the *platinichloride*,



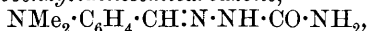
crystallises in yellow needles and melts and decomposes at 195° (corr.).

p-Dimethylaminotriphenylmethane, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2$, is prepared in the same manner by the action of *p*-dimethylaminobenzaldehyde on magnesium phenyl bromide.

4-Diethylamino-1- α -ethylpropylbenzene, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHEt}_2$, prepared in the same manner by the action of *p*-diethylaminobenzaldehyde on magnesium and ethyl bromide, is obtained as an oil which boils at $140\text{--}141^\circ$ under 7 mm., or at 278° (corr.) under 760\cdot5 mm. pressure, and has a sp. gr. $0\cdot90584$ at $21^\circ/21^\circ$, n_D $1\cdot5209$ at 21° .

The *hydrochloride* forms a strongly hygroscopic syrup; the *platinichloride* forms golden, prismatic crystals and decomposes at 179° (corr.); the *methiodide* is an oil.

p-Dimethylaminobenzylidenesemicarbazone,



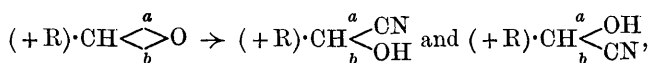
crystallises in yellow leaflets and melts and decomposes at 224° (corr.). *p*-Dimethylaminothiobenzamide, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CS} \cdot \text{NH}_2$, formed by the action of hydrogen sulphide on *p*-dimethylaminobenzonitrile dissolved in alcoholic ammonia, crystallises in yellow needles, sinters at 170° , and melts and decomposes at 209° (corr.). *p*-Diethylaminobenzylidenesemicarbazone, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, crystallises in glistening, yellow scales and melts and decomposes at 214° (corr.). *p*-Diethylaminobenzylideneaniline, $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{NPh}$, crystallises in large, glistening, yellow scales and melts at $108\text{--}109^\circ$. G. Y.

Giustiniani's Benzylmalimide. OSKAR LUTZ (*J. pr. Chem.*, 1905, [ii], 71, 34—38. Compare Abstr., 1904, i, 831; Giustiniani, Abstr., 1892, 820; Ladenburg and Hertz, Abstr., 1897, i, 460).—Polemical. A reply to Ladenburg and Herz (Abstr., 1904, i, 992). G. Y.

4 : 4'-Diaminoformyl- (acetyl) -diphenylamine. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 156388).—4 : 4'-Dinitroformyldiphenylamine, $\text{COH} \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, prepared by nitrating formyldiphenylamine in concentrated sulphuric acid solution, separates from hot formic acid in small crystals and melts at 159° . This and the corresponding acetyl compound are reduced by iron and a small quantity of sulphuric acid, the bases formed being extracted with dilute sulphuric acid and precipitated by addition of sodium acetate. The sulphates, unlike that of 4 : 4'-diaminodiphenylamine, dissolve readily in water.

4 : 4'-Diaminoformyldiphenylamine, $\text{COH} \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2$, separates from alcohol in small crystals and melts at 193° ; 4 : 4'-diaminoacetyl-diphenylamine melts at 195° . The bases yield tetrazonium compounds, from which azo-dyes may be prepared. C. H. D.

Stereochemical Studies. I. New Method of Separating Racemic Compounds. EMIL ERLÉNMEYER, jun., and ALFRED ARNOLD (*Annalen*, 1904, **337**, 307—328).—After a *résumé* of the methods at present in use for separating racemic compounds into their active components, Pasteur's use of an active base (or acid) to separate a racemic acid (or base) is discussed. In this case, two semi-racemic salts, $++$ and $-+$, are formed, which can generally be separated by considerable difference in solubility. Such semiracemic compounds should also be formed in other reactions between a racemic and an active substance, for example, between hydrocyanic acid and active aldehydes. In this case, the racemic carbon atom is produced in the reaction. Representing the two linkings of the carbonyl group by a and b respectively, thus :

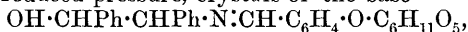


a semiracemic compound is formed which can be separated into its constituents by taking advantage of different solubilities, &c. If R is symmetric, as in benzaldehyde, equal numbers of $+$ and $-$ molecules are produced. If R is asymmetric, different numbers of $+$ and $-$ molecules are produced, as, for example, in the reduction of *d*-benzoin, where the carbonyl group becomes reduced, only hydrobenzoin and no *isohydrobenzoin* is formed, hence a selective reduction of one only of the links of the group occurs.

On applying these views to the separating of racemic bases into their active constituents, it was found possible to obtain the $+$ and $-$ forms of *isodiphenylhydroxyethylamine* by causing it to react with the active aldehyde, helicin, and separating the two condensation products by their different solubilities.

The hydrochloride of the *d*-base melts at 228° and has $[\alpha]_D$ 80.23° ; the hydrochloride of the *l*-base has the same melting point, and both are more easily soluble in methyl alcohol than the *r*-salt. In addition to the tartrates of the *d*- and *l*-bases previously described, the neutral tartrate of the *r*-base, melting at $212\text{--}214^\circ$, has been isolated.

On fractionally evaporating the alcoholic solutions of the *r*-base and helicin under reduced pressure, crystals of the base



separate; this is the compound of helicin and the *d*-base, the corresponding compound of helicin and the *l*-base being deposited as an amorphous mass from the mother liquor. The derivative of the *d*-base crystallises in colourless needles melting at 189° , and has $[\alpha]_D$ -6.43° , whilst the derivative of the *l*-base melts at 90° , is hygroscopic, and has $[\alpha]_D$ -43.6° . The active bases were obtained by hydrolysing these compounds with dilute hydrochloric acid. The *d*-base crystallised in needles melting at $113\text{--}114^\circ$, and had $[\alpha]_D$ -109.72° , whilst the *l*-base formed crystals melting at 114° , was slightly less soluble than the *d*-base, and had $[\alpha]_D$ -108° . The solubility of the *r*-base in alcohol was only one-third of that of the active bases.

K. J. P. O.

New Isomerism of Ethylene Derivatives. EMIL ERLÉNMEYER, jun., and ALFRED ARNOLD (*Annalen*, 1904, 337, 329—353. Compare preceding abstract).—In substances of the type $CR_1R_2:CR_1R_3$, which can exist in two geometric isomerides, transformation of the labile into the stable form can undoubtedly occur directly, by a simple revolution of the linking between the carbon atoms and without any addition to the ethylene linkage. It can be shown that in this revolution, there are two intermediate positions, in which the attractive forces causing the revolution are in equilibrium; these two positions must therefore have the same stability. Further, it can be shown that these two positions bear to one another the relation of object to image if the four groups R_1, R_2, R_1, R_3 are supposed to occupy the four angles of a tetrahedra.

Applying these considerations to the isomerism of the cinnamic acids, it is suggested that *allocinnamic* acid, which crystallises in hemihedric forms, is a racemic compound of the two stereoisomerides. Possibly Liebermann's *isocinnamic* acid is one of these isomerides, whilst Erlenmeyer's *isocinnamic* acid is the geometric isomeride of ordinary cinnamic acid.

It is doubtful whether these stereoisomerides would be optically active, but their asymmetry would have an effect when they were combined with an asymmetric substance. Such an example appears to exist in the compounds of *isodiphenylhydroxyethylamine* and cinnamaldehyde. Since isomeric compounds appear to be formed from cinnamaldehyde and hippuric acid, it is possible that the aldehyde is itself composite. Cinnamaldehyde and *l-isodiphenylhydroxyethylamine* yield two isomeric dextrorotatory compounds, whilst the *d-base* yields another pair of levorotatory compounds, five modifications with the inactive form altogether existing.

r-isoDiphenylhydroxyethylamine and cinnamaldehyde, when mixed in mol. proportions in alcoholic solution, yield a precipitate of the compound $OH \cdot CHPh \cdot CHPh \cdot N : CH \cdot CH : CHPh$, which forms colourless crystals melting and decomposing at 185° ; it is decomposed into its constituents by dilute sulphuric acid. The *l-base* gives a similar substance, representing 50 per cent. of the material used; it is sparingly soluble, melts and decomposes at 190° , and is dextrorotatory; from the mother liquor, an isomeric substance is obtained which forms pale yellow crystals melting at 131° and having $[\alpha]_D + 52.56^\circ$ in alcoholic solution. The *d-base* yields a similar pair of substances of similar properties, but levorotatory, $[\alpha]_D - 52.12^\circ$ in alcoholic solution. The solubility of the three substances of higher melting point in 100 parts of alcohol are, compound from *r-base* (m. p. 185°) 0.12 part, compound from *d-base* (m. p. 190°) 0.174 part, and compound from *l-base* (m. p. 190°) 0.178 part.

Derivatives of Racemic and Optically Active isoDiphenylhydroxyethylamine.—The benzylidene compound of the *d-base*, prepared from the components in alcoholic solution, crystallises in colourless needles melting at 137° and having $[\alpha]_D + 55.53^\circ$ in alcohol solution; the benzylidene compound of the *l-base* melted at 137° and had $[\alpha]_D - 56.00^\circ$. The compound from salicylaldehyde and the *r-base* forms pale yellow crystals melting at 113° . The anisaldehyde compound of the

r-base crystallises in colourless needles melting at 145° , the vanillin compound forms yellow, cubical crystals melting at 148° , the piperonal compound colourless needles melting at 131° , and the *p*-nitrobenzaldehyde compound yellow needles melting at 132° . Ethyl acetoacetate condenses with the *r*-base, forming yellow, rhombic crystals melting at 145° ; the similar compound from pyruvic acid and the *r*-base forms crystals melting and decomposing at 152° ; the analogous compound with the *d*-base is insoluble, melts at 161° , and has $[\alpha]_D + 88.82^{\circ}$ in alcoholic solution, whilst the derivative of the *l*-base, which melts at 161° , has $[\alpha]_D - 87.71^{\circ}$. The *acetyl* derivative of the *r*-base crystallises in colourless needles melting at 152° , and yields a *hydrochloride* melting at 193° ; no diacetyl derivative could be obtained. The *d-acetyl* derivative melts at 159° , has $[\alpha]_D + 12.74^{\circ}$, and forms a *hydrochloride* melting at $196-197^{\circ}$. The *l-acetyl* derivative has $[\alpha]_D - 12.80^{\circ}$. The *r-benzoyl* derivative, prepared by the action of benzoyl chloride in benzene solution, crystallises in needles melting at 223° ; the *d-benzoyl* derivative forms needles melting at 215° and having $[\alpha]_D + 29.02^{\circ}$ in methyl-alcoholic solution, and the *l-benzoyl* derivative melting at $214-215^{\circ}$, $[\alpha]_D - 29.00^{\circ}$. The *r-dibenzoyl* derivative, prepared by boiling the base with benzoyl chloride, is a powder melting at 187° and is identical with the compound obtained from diphenyl-hydroxyethylamine, a fact which shows that the latter changes partly into the *iso*-compound on benzoylating.

The hydrochloride of the *r*-base yields with potassium cyanate the compound $\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which separates from acetone in crystals containing acetone, and melts when dry at 157° .

K. J. P. O.

Action of Phosphorus Pentachloride on Tertiary Cyclic Amines. Synthesis of Dyes and Formation of Phosphorus. PAUL LEMOULT (*Compt. rend.*, 1905, 140, 248—250. Compare Abstr., 1904, i, 380, 806, 807; this vol., i, 48).—Phosphorus pentachloride yields a deep blue coloration with dimethylaniline (compare Michler and Walden, Abstr., 1882, 175), which disappears on boiling, methyl chloride being evolved; if, however, the temperature is maintained at 80° to 100° , there is no evolution of gas, and the solid product, which is deeply coloured, consists of (1) tetramethyldiaminodiphenylmethane; (2) hexamethyltriaminotriphenylmethane, the leuco-base of hexamethyl-violet; (3) the compound $\text{PO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$, not yet described, but which gives with alcohol the compound $\text{PO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3\cdot\text{EtOH}$, obtained by Michaelis and von Soden (Abstr., 1885, 1134); and (4) an orange-yellow substance containing free phosphorus. Colouring matters were also obtained when methylethylaniline, dimethyl-*o*-toluidine, benzylmethylaniline, or diphenylmethylaniline replace the dimethylamine in the above reaction, but dimethyl-*p*-toluidine, diethylaniline, or benzyethylaniline do not give coloured products with phosphorus pentachloride. These facts show that only those tertiary cyclic amines in which the para-position of the aryl radicle is free and which contain at least one methyl group are capable of giving synthetical dyes with phosphorus pentachloride.

M. A. W.

Phenylcarbimide as a Reagent for Determining the Constitution of Tautomeric Compounds. ARTHUR MICHAEL (*Ber.*, 1905, **38**, 22—49. Compare Dieckmann, Hoppe, and Stein, this vol., i, 135).—The author has studied the action of phenylcarbimide on compounds showing enol-keto-tautomerism and their sodium derivatives, with a view to determining the influence of the more or less acid character of the compounds concerned on the course of the reaction. In the case of sodium derivatives, phenylcarbimide forms an additive product whenever the nature of the parent compound is such that the sodium is "more fully neutralised" in the additive product than in the original compound (*Abstr.*, 1900, i, 321; 1904, ii, 164). When this is not the case, polymerisation to triphenyl *isocyanurate* (Hofmann, *Ber.*, 1870, **3**, 268) takes place, often accompanied by secondary decompositions.

Thus sodium ethoxide and the sodium derivatives of ethyl α -formylpropionate, formylcamphor, and ethyl formylphenylacetate only cause polymerisation of the phenylcarbimide, phenylurethane being also formed under certain conditions.

Phenylcarbimide reacts with the sodium or copper derivative of ethyl acetoacetate in ether at the ordinary temperature to form a *C-additive compound*, $\text{ONa} \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$. Acids set free the hydroxylic compound, crystallising from alcohol in large prisms and melting at 57° (compare Dieckmann, *Abstr.*, 1900, i, 482). The *semicarbazone* melts at 152 — 154° and is converted into a *compound* melting at 210 — 220° by crystallisation from water. Potassium hydroxide hydrolyses it to the monoanilide of malonic acid.

Ethyl sodiomalonate and phenylcarbimide react vigorously in ether to form a *C-compound*, $\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}$, crystallising from alcohol in long, white, prismatic needles and melting at 126° . The *sodium* salt is hydrolysed by water, and dissolves only in an excess of sodium hydroxide.

Ethyl sodiobenzoylacetate yields an additive compound, $\text{C}_{18}\text{H}_{17}\text{O}_4\text{N}$, crystallising in white, prismatic needles melting at 145 — 146° , but previously softening. This compound is neutral, but dissolves in alkali hydroxides on heating, and acids then precipitate the white, labile enolic form, which dissolves readily in alkaline solutions, but passes gradually into the stable ketonic form (compare Wislicenus, *Abstr.*, 1899, i, 60; Ruhemann and Watson, *Trans.*, 1904, **85**, 456).

Sodiodiacetylmethane yields an *additive compound*, $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}$, crystallising from water in prismatic needles melting at 118 — 120° . It dissolves readily in alkali carbonates and is reprecipitated by acids. The enolic form has no tendency to ketonise. Alkali hydroxide decomposes it, forming acetoacetanilide.

Ethyl sodioformylacetate yields an *enolic additive compound*, $\text{OH} \cdot \text{CH} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$, crystallising from alcohol in white prisms melting at 52 — 53° . The *sodium* salt, $\text{C}_{12}\text{H}_{12}\text{O}_4\text{NNa} \cdot 2\text{H}_2\text{O}$, forms white crystals, moderately soluble in water. The *phenylhydrazone* forms white prisms melting at 136 — 137° .

In the reaction between ethyl sodioethylmalonate and phenylcarbimide, one carbethoxy-group is eliminated, and a *compound*,

$C_{25}H_{21}O_4N_3$, is formed, crystallising from benzene in rounded groups of small prisms melting at $141-142^\circ$ and behaving as a weak monobasic acid. The *silver* salt forms white, prismatic needles. The same compound is obtained from ethyl ethylacetoacetate and phenylcarbimide. The *product* from ethyl sodiomethylmalonate melts at $198-200^\circ$.

Sodionitromethane and phenylcarbimide react together only slowly, forming *nitroacetanilide*, $NO_2 \cdot CH_2 \cdot CO \cdot NHPh$, crystallising from water in bright yellow, feathery leaflets melting at $138-139^\circ$ and dissolving readily in alcohol, ether, chloroform, or benzene, together with *nitromalonanilide*, $NO_2 \cdot CH(CO \cdot NHPh)_2$, crystallising from alcohol in pale yellow leaflets melting at $141-142^\circ$.

Potassium nitroform does not react with phenylcarbimide.

The conclusion drawn by Goldschmidt and Meissler (Abstr., 1890, 499) that only enolic compounds form additive products on heating with phenylcarbimide is not justified. Acetophenone, ethyl malonate, ethyl ethylmalonate, and ethyl oxaloacetate do not react with phenylcarbimide at 100° . Ethyl ethylacetoacetate reacts at 180° , forming an oil boiling at $190-210^\circ$ under 17 mm. pressure. In the series of compounds next examined, the reaction takes place more readily with increasing acidity of the compound employed. An accumulation of ketonic groups hinders the reaction, even when an enolic group is present.

Ethyl acetoacetate, diacetylmethane, and ethyl benzoylacetate yield the same additive products as their sodium derivatives. Dibenzoylmethane reacts with phenylcarbimide in ethereal solution at the ordinary temperature, the product melting at $195-196^\circ$ or $205-207^\circ$, according to the time of heating (compare Wislicenus, *loc. cit.*).

Ethyl α -formylpropionate reacts readily to form the *compound* $CHO \cdot CMe(CO_2Et) \cdot CO \cdot NHPh$, crystallising from benzene in colourless, glistening, prismatic needles melting at $117-119^\circ$. It is insoluble in alkali hydroxides, but is slowly decomposed by them, forming α -formylpropionanilide, $C_{10}H_{11}O_2N$, melting at $82-87^\circ$. Semicarbazide acetate reacts with it to form a crystalline *compound* of unknown constitution, melting at $231-232^\circ$.

Both ethyl α - and β -formylphenylacetates react readily with phenylcarbimide, the products melting at 59° and 116° respectively. This result is contrary to the statement of W. Wislicenus (Abstr., 1896, i, 552), and is being further investigated.

Nitroethane and nitromethane do not react below 140° , great decomposition then taking place.

Dibenzoylacetylmethane and its enolic isomeride do not yield additive products with phenylcarbimide. The former yields a *compound* melting at $118-122^\circ$ and not containing nitrogen. Enolic benzoyldiacetylmethane yields a *compound* containing nitrogen, which is being further investigated.

Phloroglucinol and phenylcarbimide react in cold ethereal solution to form a *compound* $C_{27}H_{21}O_6N_3$, crystallising from alcohol or benzene in white, prismatic needles melting at $190-192^\circ$, and isomeric with the compound obtained by Goldschmidt and Meissler (Abstr., 1890, 499).

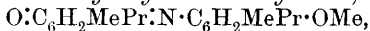
C. H. D.

Thymomenthol [Hexahydrothymol] and its Derivatives.

LÉON BRUNEL (*Compt. rend.*, 1905, **140**, 252—253).—Hexahydrothymol (for which the author suggests the name thymomenthol to recall its origin and its close relationship to menthol) is more conveniently prepared by the direct hydrogenation of thymol in the presence of reduced nickel at 160° than at 180—185° (compare Abstr., 1904, i, 158), the amount of acetone formed (compare Sabatier and Senderens, Abstr., 1903, i, 454) being much less at the lower temperature. Pure thymomenthol is a syrupy, colourless liquid with a strong odour of mint, has a sp. gr. 0.913 at 0°, melts between -5° and 0°, boils at 215.5° under atmospheric pressure, is insoluble in water, readily soluble in alcohol, ether, or acetic acid, volatilises rapidly at the ordinary temperature, and is converted into *tetrahydrocymene* (thymomenthene) by the action of phosphoric oxide or potassium hydrogen sulphate; the new hydrocarbon closely resembles menthene, having a sp. gr. 0.823 at 0° and boiling at 167—168°, whilst the corresponding values for menthene are 0.8266 and 167.4°. The esters of thymomenthol are readily prepared by heating the alcohol with excess of the acid anhydride, or by heating molecular proportions of the alcohol and acid anhydride with pyridine, or by the action of the acid anhydride on the sodium derivative of the alcohol; they yield on hydrolysis β -thymomenthol, which is a stereoisomeride of the original or α -compound, and crystallises in long, colourless needles melting at 28° and boiling at 217° under atmospheric pressure, is readily soluble in alcohol, ether, acetone, light petroleum, or acetic acid, insoluble in water, and is much less volatile than the α -isomeride. β -Thymomenthyl hydrogen succinate, $\text{CO}_2\text{H}\cdot\text{C}_2\text{H}_4\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, crystallises in thin, colourless, odourless needles melting at 80°, soluble in alcohol and in warm light petroleum. β -Thymomenthyl hydrogen phthalate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, crystallises in large, colourless, odourless prisms melting at 128°, readily soluble in alcohol or chloroform.

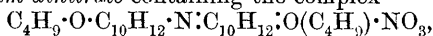
M. A. W.

Nitrosophenol Dyes. III. HERMAN DECKER and BORIS SOLONINA (*Ber.*, 1905, **38**, 64—68; 720. Compare Abstr., 1902, i, 767; 1903, i, 838).—When crude nitric acid is added to a solution of thymol methyl ether in acetic acid, a dark blue, uncrystallisable solution of an oxonium salt is obtained (compare Kehrman, Abstr., 1902, i, 767). On reducing at 0° with stannous chloride and hydrochloric acid and decomposing the stannochloride formed, *dithymolylamine dimethyl ether*, $\text{NH}(\text{C}_6\text{H}_2\text{MePr}\cdot\text{OMe})_2$, is obtained, melting at 88.5—89° after crystallisation from alcohol. The *hydrochloride* forms white needles, commencing to melt at 140°; the *hydriodide* forms white needles melting indistinctly at 136°. Ferric chloride oxidises the ether in alcoholic solution to *thymoquinonethymolylimide methyl ether*,



crystallising from methyl alcohol in red needles and melting at 66—67°. Stannous chloride reduces it quantitatively to *dithymolylamine methyl ether*. The same red indophenol ether may be prepared by the action of nitroso-sulphuric acid on thymol and methylation of the product by means of methyl sulphate.

Thymol *n*-butyl ether and nitric acid react in acetic acid solution to form an *oxonium dinitrate* containing the complex



the other NO_3 group being probably attached to the nitrogen atom. The salt forms bronze crystals melting at 66° , and is more stable than the ethyl derivative obtained by Kehrmann. *Dithymolylamine dibutyl ether*, $\text{C}_{28}\text{H}_{48}\text{O}_2\text{N}$, forms bright yellow crystals melting at $69\cdot5^\circ$; the *hydrochloride* forms white needles and melts at 107° . *Thymoquinone-thymolylimide n-butyl ether*, $\text{C}_{24}\text{H}_{33}\text{O}_2\text{N}$, crystallises in red prisms and melts at 55° .

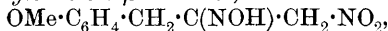
The same colour-reactions (formation of blue oxonium salt and red indophenol ether) were observed in the case of thymol *isopropyl ether* and *p*-xylenol ethyl and methyl ethers.

C. H. D.

Myristicin. I. ENRICO RIMINI (*Gazzetta*, 1904, **34**, ii, 281—300).

—In order to ascertain whether Angeli's method of detecting the presence of an allyl group by the action of nitrous acid is of general applicability, the author has tested it on a number of compounds. It is found that nitrous acid reacts with all compounds containing an allyl group as a side-chain, but with much greater difficulty than with those having a propenyl side group. The reaction can, however, be employed to distinguish allyl compounds from propenyl compounds, since the nitrosites obtained yield, in the former case, nitro-oximes, and in the latter peroxides of dioximes. From the behaviour of myristicin and *isomyristicin* towards nitrous acid and towards mercuric acetate, it is concluded that the former contains an allyl side-chain and the latter a propenyl side-chain.

Methylchavicol α -nitrosite, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_5\cdot\text{N}_2\text{O}_3$, prepared by the action of nitrous acid on methylchavicol in light petroleum solution, forms a pale lemon-yellow powder melting and decomposing at 147° . On boiling with absolute alcohol in a reflux apparatus until dissolved, it passes into *methylchavicol β -nitrosite*,



which is deposited from benzene in white crystals melting at 112° .

p-*Methoxyphenylnitroacetone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$, obtained by boiling the preceding compound with dilute sulphuric acid, crystallises from alcohol in shining, white scales melting at 89° . On oxidation with dilute alkaline permanganate solution, it yields anisic and homoanisic acids. On gentle reduction with stannous chloride and hydrochloric acid in alcoholic solution, it gives *p*-*methoxyphenylaminoacetone hydrochloride*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$, which crystallises from alcohol in shining, white laminae melting and decomposing at 198 — 199° . The corresponding *picrate*,



crystallises from alcohol in orange-yellow needles decomposing at 148° .

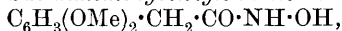
2:5-*Di-p-anisylpyrazine*,



prepared by the action of ammonia on *p*-methoxyphenylaminoacetone

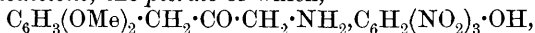
hydrochloride, is deposited from aqueous alcohol as a white, crystalline powder melting and decomposing at about 150° .

Methyleugenol α -nitrosite, $C_6H_3(OMe)_2 \cdot C_3H_5 \cdot N_2O_3$, which is only obtainable with difficulty, forms a lemon-yellow powder, melting and decomposing at 130° . When boiled with alcohol, a syrupy β -nitrosite is formed, and this, with dilute sulphuric acid, gives *dimethoxyphenylnitroacetone*, $C_6H_3(OMe)_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot NO_2$, which crystallises from alcohol in plates melting at 103° . On treatment with hydroxylamine in presence of sodium carbonate and hydroxide, this does not give the nitroxime expected, but *dimethoxybenzylloxamic acid*,



which separates from alcohol in mammillary aggregates melting and decomposing at 137° , and gives a violet coloration with ferric chloride and a bottle-green precipitate with copper acetate.

When reduced, dimethoxyphenylnitroacetone yields *dimethoxyphenylaminoacetone*, the *picrate* of which,

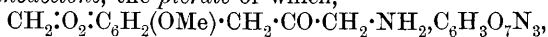


separates from alcohol in crystals melting and decomposing at 153° .

Apiole α -nitrosite, $CH_2 \cdot O_2 \cdot C_6H(OMe)_2 \cdot C_3H_5 \cdot N_2O_3$, prepared only with great difficulty and in small yield, is a lemon-yellow powder, which melts and decomposes at about 138° and is insoluble in all ordinary solvents. *Dill-apiole α -nitrosite* melts and decomposes at 139° .

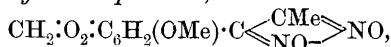
Myristicin α -nitrosite, $CH_2 \cdot O_2 \cdot C_6H_2(OMe) \cdot C_3H_5 \cdot N_2O_3$, formed, together with a large proportion of resin, from myristicin and nitrous acid, is a yellow powder melting and decomposing at 130° . The β -nitrosite could only be obtained as a syrup, which, when treated with dilute sulphuric acid, yields *methoxymethylenedioxyphenylnitroacetone*, $CH_2 \cdot O_2 \cdot C_6H_2(OMe) \cdot CH_2 \cdot CO \cdot CH_2 \cdot NO_2$, crystallising from alcohol in shining scales melting at 132 – 133° .

On reduction, the foregoing compound yields *methoxymethylenedioxyphenylaminoacetone*, the *picrate* of which,



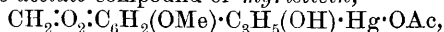
separates from alcohol in crystals melting and evolving gas at 182° .

Diisonitrosoisomyristicin peroxide,



prepared by the action of nitrous acid on *isomyristicin*, is deposited from alcohol in shining, yellow crystals melting at 103° . Reduction by means of zinc dust and acetic acid in alcoholic solution yields *diisonitrosoisomyristicin*, $CH_2 \cdot O_2 \cdot C_6H_2(OMe) \cdot C(NO_2) \cdot CMe \cdot NOH$, which separates from aqueous alcohol in white crystals melting at 136° .

The *mercuric acetate* compound of *myristicin*,



prepared, together with a non-crystalline *isomeride*, by treating a benzene solution of myristicin (1 mol.) with a saturated aqueous solution of mercuric acetate (1 mol.), crystallises from benzene in white, mammillary masses melting at 111° . Treatment of an aqueous solution of this compound (1 mol.) with saturated potassium chloride (1 mol.) solution yields the compound $C_{11}H_{13}O_4ClHg$, separating from alcohol in white crystals melting at 127° .

Dihydroxyisomyristicin, $CH_2 \cdot O_2 \cdot C_6H_2(OMe) \cdot C_3H_5(OH)_2$, obtained by

the prolonged action of a saturated aqueous solution of mercuric acetate (4 mols.) on a benzene solution of *isomyristicin* (1 mol.), with subsequent reduction by means of zinc and potassium hydroxide solution, crystallises from ether in mammillary masses melting at 114—115°.

isoMyristicin picrate, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_2(\text{OMe})\cdot\text{C}_8\text{H}_5\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from alcohol in red needles melting at 86°. The ready formation of such a compound is characteristic of all propenyl compounds, especially those containing a methylenedioxy-group (compare Bruni and Tornani, Abstr., 1904, i, 875). T. H. P.

Condensation of Nitromalonaldehyde with Benzyl Methyl Ketone. HENRY B. HILL and WILLIAM J. HALE (*Amer. Chem. J.*, 1905, 33, 1—21).—When benzyl methyl ketone reacts with the sodium derivative of nitromalonaldehyde, 5-nitro-2-hydroxydiphenyl is produced, which melts at 125—126° (corr.) (compare Borsche, Abstr., 1900, i, 594); its *sodium* derivative crystallises with $3\frac{1}{2}\text{H}_2\text{O}$. The *methyl ether* of 5-nitro-2-hydroxydiphenyl crystallises in colourless needles and melts at 95·2° (corr.); the *ethyl ether* melts at 110·6° (corr.), and the *benzoyl* derivative forms small, white, irregular prisms and melts at 99·3° (corr.).

5-Amino-2-hydroxydiphenyl melts at 199° (corr.), diphenylquinone melts at 112—113° (corr.), and 3:5-dinitro-2-hydroxydiphenyl melts at 207—208° (corr.) (compare Borsche, Abstr., 1900, i, 24).

The *sodium* derivative of 3:5-dinitro-2-hydroxydiphenyl crystallises with $2\text{H}_2\text{O}$; the *methyl ether* crystallises in colourless leaflets and melts at 114—115° (corr.). When 3:5-dinitro-2-hydroxydiphenyl is reduced with tin and hydrochloric acid, the *hydrochloride* of 3:5-diamino-2-hydroxydiphenyl is produced, which forms colourless crystals; on treating this compound with potassium carbonate, a yellow, flocculent precipitate of the *base* is obtained, which becomes reddish-brown when dry, and is soluble in alcohol or glacial acetic acid.

On oxidising the methyl ether of 5-nitro-2-hydroxydiphenyl with a solution of chromium trioxide in glacial acetic acid, the methyl ether of 5-nitrosalicylic acid is produced, together with benzoic acid. The methyl ether of 3:5-dinitro-2-hydroxydiphenyl is oxidised by chromic acid with considerable difficulty, small quantities of the methyl ether of 3:5-dinitrosalicylic acid being produced.

When either 5-nitro-2-hydroxydiphenyl or 3:5-dinitro-2-hydroxydiphenyl is boiled with nitric acid of sp. gr. 1·40, carbon dioxide is evolved and *p*-nitrobenzoic acid is produced.

By the action of nitric acid of sp. gr. 1·40 on the methyl ether of 3:5-dinitro-2-hydroxydiphenyl, the *methyl ether* of 3:5:4'-trinitro-2-hydroxydiphenyl, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OMe}$, is produced, which crystallises in prisms and melts at 170—171° (corr.). 3:5:4'-*Trinitro-2-hydroxydiphenyl*, obtained by hydrolysing the methyl ether with concentrated hydrochloric acid, crystallises in pale yellow prisms, melts at 163—164° (corr.), is readily soluble in benzene, ether, or chloroform, and fairly so in glacial acetic acid or carbon disulphide, and on oxidation with nitric acid yields *p*-nitrobenzoic acid; the *sodium* salt forms orange-red crystals.

When 5-nitro-2-hydroxydiphenyl methyl ether is boiled with a mixture of nitric and glacial acetic acids, the *methyl ether* of 5 : 4'-dinitro-2-hydroxydiphenyl, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OMe}$, is produced, which crystallises in white, slender needles and melts at $222-223^\circ$ (corr.); on hydrolysis with concentrated hydrochloric acid, it is converted into 5 : 4'-dinitro-2-hydroxydiphenyl, which crystallises in long, slender, pale yellow needles, melts at $224-225^\circ$ (corr.), is readily soluble in alcohol, ether, chloroform, or glacial acetic acid and moderately so in hot benzene, and on oxidation with nitric acid is converted into *p*-nitrobenzoic acid; the *sodium* salt crystallises in orange-red needles.

By the action of nitric acid of sp. gr. 1.40 on 5-nitro-2-hydroxydiphenyl methyl ether, the methyl ether of 3 : 5 : 4'-trinitro-2-hydroxydiphenyl is produced together with the *methyl ether* of the corresponding 5 : 2' : 4'-trinitro-derivative, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OMe}$; the latter compound crystallises in small flattened prisms and melts at $104-106^\circ$ (corr.). 5 : 2' : 4'-Trinitro-2-hydroxydiphenyl, obtained by hydrolysing the methyl ether with concentrated hydrochloric acid, crystallises in small, pointed, yellow prisms, melts at $152-153^\circ$ (corr.), is readily soluble in chloroform and fairly so in glacial acetic acid, warm alcohol, or warm benzene, and on oxidation with nitric acid of sp. gr. 1.40 is converted into 2 : 4-dinitrobenzoic acid; the *sodium* derivative crystallises in orange-red needles. E. G.

A Correction [α -Nitrosoresorcinol Monoethyl Ethers]. FERDINAND HENRICH (*J. pr. Chem.*, 1905, [ii], 71, 56. Compare Abstr., 1904, i, 1006).—The author misunderstood Wegscheider's views as to the nature of the two modifications of α -nitrosoresorcinol monoethyl ether (*Verh. deut. Naturf. Ärzte in Kassel*) and now finds them to agree with his own (*loc. cit.*). G. Y.

Oxidation Products of Octohydroanthracene. MARCEL GODCHOT (*Compt. rend.*, 1905, 140, 250-252).—Octohydroanthracene (Abstr., 1904, i, 987) is readily oxidised by chromic acid to anthraquinone, but when the oxidation is effected in acetic acid solution at the ordinary temperature *dihydro-oxanthranol* and *hexahydroanthrone* are obtained. *Dihydro-oxanthranol*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{C}(\text{OH}) \\ \text{C}(\text{OH}) \end{smallmatrix} \right\rangle \text{C}_6\text{H}_6$, crystallises from alcohol in large, yellow, prismatic needles melting at 159° , dissolves readily in hot alcohol, benzene, toluene, or acetic acid, is not fluorescent, and its solutions give a deep red coloration with alkalis. *Diacetyldihydro-oxanthranol*, $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{C}(\text{OAc}) \\ \text{C}(\text{OAc}) \end{smallmatrix} \right\rangle \text{C}_6\text{H}_6$, crystallises in large, colourless needles melting at 220° , and soluble in hot alcohol, benzene, or acetic acid, the solutions in alcohol or acetic acid exhibiting a beautiful blue fluorescence. *Hexahydroanthrone*, $\text{C}_{14}\text{H}_{16}\text{O}$, crystallises in hard, clear plates, melts at 45.5° , boils at $222-225^\circ$ under 25 mm. pressure, is readily soluble in all the ordinary organic solvents, slightly volatile with steam, and reduces Fehling's solution or ammoniacal silver nitrate. The *semicarbazone* crystallises in small, yellow, leafy crystals melting at 250° . Dibromohexahydroanthrone, $\text{C}_{14}\text{H}_{14}\text{OBr}_2$, forms prismatic crystals melting at $123-124^\circ$, readily soluble in alcohol, carbon bisulphide, or ether. M. A. W.

p-Dimethylaminobenzaldehyde. III. Action of Magnesium Organic Compounds. FRANZ SACHS and LUDWIG SACHS (*Ber.*, 1905, **38**, 511—517. Compare *Abstr.*, 1903, i, 37; 1904, i, 506).—*p*-Dimethylaminophenylmethylcarbinol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHMe} \cdot \text{OH}$, formed by the action of 1 mol. of *p*-dimethylaminobenzaldehyde on 1 mol. of magnesium and two mols. of methyl iodide in ethereal solution, crystallises in lemon-coloured, microscopic, prismatic, pointed leaflets, melts at 60.25° , is easily soluble in water and the usual organic solvents, and dissolves in concentrated sulphuric acid to a yellow solution, and in glacial acetic acid to a yellow solution which becomes green when heated; the *hydrochloride* is obtained as a white, flocculent, hygroscopic precipitate; the *platinichloride* forms a brownish-yellow, flocculent mass. Attempts to prepare the corresponding styrene by distillation of the carbinol, or by conversion into the chloride and heating with pyridine, or by treatment with either excess of magnesium methyl iodide or acetic anhydride were unsuccessful, chiefly owing to the formation of decomposition and polymerisation products.

p-Dimethylaminophenylethylcarbinol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHEt} \cdot \text{OH}$, formed by the action of *p*-dimethylaminobenzaldehyde on magnesium ethyl bromide in well-cooled ethereal solution, crystallises in needles, melts at 46° , gradually decomposes at the ordinary temperature, and is only slightly soluble in water, but easily so in the ordinary organic solvents; the *platinichloride* forms a yellow oil. When heated under 10 mm. pressure, the carbinol yields 4-dimethylamino-1- Δ^a -propenylbenzene (*p*-dimethylaminophenylpropylene), which distils at 152 — 154° , crystallises in microscopic, white needles, slowly decomposes at the ordinary temperature, and dissolves in concentrated sulphuric acid to a golden, in hot glacial acetic acid to a bluish-green, solution; the *platinichloride* crystallises in broad, yellow needles and melts at 132° .

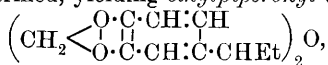
p-Dimethylaminophenylbenzylcarbinol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Ph}$, prepared by the action of the aldehyde on magnesium and benzyl chloride, crystallises in sheaves of white needles, melts at 59 — 60° , has a bitter flavour, and forms an oily *platinichloride*. *p*-Dimethylaminostilbene, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CHPh}$, is formed on prolonged boiling of the carbinol in alcohol, or on heating the carbinol under 10 mm. pressure, when the stilbene distils at 251 — 252° . It crystallises in broad, glistening leaflets and melts at 147 — 148° . The *hydrochloride* crystallises in small, white leaflets and melts and decomposes at 174 — 175° ; the *platinichloride* crystallises in small, colourless needles, rapidly becomes rust-coloured, and melts and decomposes at 168° ; the *picrate* crystallises in brown, microscopic needles and melts at 158° ; the *methiodide* crystallises in yellow leaflets and melts at 204° (corr.).

p-Dimethylaminophenyl- α -naphthylcarbinol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{C}_{10}\text{H}_7$, prepared by the action of the aldehyde on magnesium and α -bromonaphthalene, crystallises in white prisms, melts at 97 — 98° , and dissolves in mineral acids to form coloured solutions. The *platinichloride* crystallises in hexagonal leaflets which remain unchanged at 230° .

s-Diphenylcarbamide was the only product obtained by the action of phenylcarbimide on the above carbinols. G. Y.

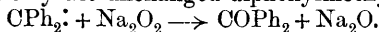
Action of Magnesium Ethyl Iodide on Piperonaldehyde.
New Synthesis of isoSafrole. EFISIO MAMELI (*Gazzetta*, 1904, 34, ii, 409—419).—Besides the work already noticed (Abstr., 1904, i, 1023), a description is given of the *benzoyl* derivative of *ethylpiperonyl-carbinol*, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHEt}\cdot\text{OBz}$, which separates from benzene in white crystals melting at 112° .
T. H. P.

Ethylpiperonyl Ether. EFISIO MAMELI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 611—614. Compare Abstr., 1904, i, 743).—When kept in an impure state, ethylpiperonylcarbinol (Abstr., 1904, i, 1023) becomes slowly etherified, yielding *ethylpiperonyl ether*,



which crystallises from benzene or alcohol in small, white prisms melting at 88°, dissolves readily in ether, light petroleum, chloroform, or pyridine, and slightly in acetic acid, and exhibits normal cryoscopic behaviour in benzene solution. It does not reduce ammoniacal silver nitrate or Fehling's solution, and does not combine with benzoyl chloride or phenylhydrazine. On treatment with concentrated sulphuric acid, the crystals become dark red, whilst the liquid assumes an intense blood-red coloration which changes to violet in a few hours. Concentrated nitric acid dissolves the ether with great energy, nitrous fumes being abundantly evolved; on adding water to the mixture, a nitro-derivative is precipitated. When heated, even under reduced pressure, the ether decomposes into water and *isosafole*; this decomposition takes place in two stages, like that of the corresponding methyl compound (*loc. cit.*).
T. H. P.

Reactions of Sodium Benzhydrol. RAYMOND FOSS BACON (*Amer. Chem. J.*, 1905, 33, 68—97).—The *sodium* derivative of benzhydrol crystallises in large, transparent, colourless plates, turns green or greenish-blue on exposure to light, but becomes colourless again in the dark; it decomposes at 250° with formation of benzene, sodium benzoate, diphenylmethane, and sometimes tetraphenylethane and tetraphenylethylene. When dry air and oxygen are passed over sodium benzhydrol at the ordinary temperature, benzophenone, sodium peroxide, sodium carbonate, and a small quantity of sodium benzoate are produced. The reaction is considered to take place between the dissociated benzhydrol molecules and the active oxygen molecules in accordance with the following scheme: $\text{CPh}_2 \cdot + 2\text{NaOH} + \text{O}_2 \longrightarrow \text{CPh}_2(\text{ONa})_2 + \text{H}_2\text{O}_2 \longrightarrow \text{COPh}_2 + \text{Na}_2\text{O}_2 + \text{H}_2\text{O}$. The amount of sodium peroxide present at the end of one experiment was found to be only 21·67 per cent. of the amount demanded by the equation, this being due to its reduction by the unchanged diphenylmethylene,



When bromodiphenylmethane is oxidised with potassium permanganate in presence of sulphuric acid, benzophenone is obtained. If dry oxygen is passed through bromodiphenylmethane at 160—170°,

hydrogen bromide is evolved and benzophenone is produced together with a small quantity of tetraphenylethylene. By the action of sodium on an ethereal solution of bromodiphenylmethane, tetraphenylethane and diphenylmethane are formed.

Conrad and Hodgkinson (Abstr., 1877, 590) have shown that when sodium reacts with benzyl acetate at 135° , benzyl acetoacetate is not produced, but the chief product is benzyl β -phenylpropionate. It is now found that benzyl ether is also formed in this reaction. The action of sodium on benzyl acetate and benzhydryl acetate in cold ethereal solution has been studied by Shaklee, who has found that the main products of the reaction are acetic acid and benzyl alcohol or benzhydrol respectively, a small amount of diacetyl being formed in each case.

Benzyl acetoacetate, which has been prepared by Shaklee by the action of benzyl alcohol on ethyl acetoacetate at 160° , is a colourless, mobile oil which boils at $162\text{--}164^{\circ}$ under 16 mm. pressure, boils and decomposes at about 270° under the ordinary pressure, and gives a blood-red coloration with alcoholic ferric chloride; its *copper* derivative melts at 156° .

Benzhydryl acetoacetate, prepared in a similar manner, crystallises in colourless plates, melts at 56° , is very soluble in most organic solvents, and gives a deep purple coloration with ferric chloride; the *copper* derivative melts at $174\text{--}176^{\circ}$.

Experiments have shown that by the action of sodium or sodium benzyloxide on benzyl acetate at 100° , only traces of benzyl acetoacetate are produced, and that similarly only very small quantities of benzhydryl acetoacetate can be obtained by the action of sodium benzhydrol on benzhydryl acetate.

$\beta\beta$ -Diphenylpropionic acid melts at 155° , instead of 151° as stated by Henderson (Trans., 1891, 59, 734). *Benzhydryl $\beta\beta$ -diphenylpropionate*, obtained by the action of bromodiphenylmethane on potassium $\beta\beta$ -diphenylpropionate at $150\text{--}160^{\circ}$, crystallises from alcohol in colourless needles, melts at 112° , and is readily soluble in benzene and sparingly so in ether.

When ethylacetanilide is heated for a considerable time with sodium benzhydrol in a sealed tube, ethylaniline, benzhydrol, benzhydryl ether, $\beta\beta$ -diphenylpropionic acid, and small quantities of benzophenone and tetraphenylethane are formed. If benzhydryl acetate is heated with quicklime in a sealed tube for 6 hours at $230\text{--}250^{\circ}$, $\beta\beta$ -diphenylpropionic acid, tetraphenylethane, benzhydryl ether, benzhydrol, and a small amount of benzophenone are produced.

By the interaction of benzhydryl acetate and sodium benzhydrol in a sealed tube at $150\text{--}160^{\circ}$, $\beta\beta$ -diphenylpropionic acid, benzhydryl $\beta\beta$ -diphenylpropionate, benzhydrol, benzhydryl ether, tetraphenylethylene, and small quantities of benzophenone and tetraphenylethane are formed. When benzhydryl acetate is heated with sodium at $130\text{--}140^{\circ}$, $\beta\beta$ -diphenylpropionic acid, benzhydrol, tetraphenylethylene, benzophenone, and traces of tetraphenylethane are produced. If sodium benzhydrol and benzhydryl acetate are heated together at $300\text{--}310^{\circ}$ in a sealed tube, $\beta\beta$ -diphenylpropionic acid (75 per cent. of the theoretical yield), diphenylmethane, benzophenone, and a small quantity of benzoic acid are produced.

Benzhydryl formate, obtained by the action of potassium formate on bromodiphenylmethane, is a colourless oil which boils at 159—160° under 10 mm. pressure. When this ester is heated with sodium benzhydrol for 8 hours in a sealed tube at 300—310°, diphenylacetic acid is produced.

Benzhydryl isobutyrate is a crystalline substance which melts at 54°, boils at 185—187° under 15 mm. pressure, and is soluble in alcohol or ether. When this compound is heated with sodium benzhydrol in a sealed tube, $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropionic acid, benzhydrol, diphenylmethane, and benzophenone are produced. The results of several experiments show that the yield of $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropionic acid never exceeds 30 per cent., and that diphenylmethane and benzophenone are always obtained owing to the decomposition of a large proportion of the sodium benzhydrol.

Nef (Abstr., 1898, i, 106) has stated that benzhydryl acetate decomposes at 300° with formation of acetic acid, tetraphenylethylene, and tetraphenylethane. On repeating this experiment, acetic acid, tetraphenylethylene, benzophenone, and diphenylmethane were obtained, but tetraphenylethane was not produced.

Benzhydryl ethyl ether is decomposed at 300° into acetaldehyde, tetraphenylethane, and benzophenone.

Fromm and Achert (Abstr., 1903, i, 340) have shown that benzyl sulphide decomposes when heated with formation of hydrogen sulphide, toluene, stilbene, thionessal (tetraphenylthiophen), and *s*-tetraphenylbutane. These results can be explained on the supposition that the benzyl sulphide first undergoes dissociation into hydrogen sulphide (1 mol.) and phenylmethylene (2 mols.) This view is supported by the fact that when benzyl chloride is heated with anhydrous potassium oxalate, *s*-tetraphenylbutane is produced.

Benzyl β -phenylpropionate is a colourless oil which boils at 190—195° under 10 mm. pressure and is rapidly hydrolysed by alcoholic potassium hydroxide at the ordinary temperature.

The action of sodium on benzyl acetate has been studied by Conrad and Hodgkinson (*loc. cit.*). On repeating their experiments, it was found that the neutral and less volatile products obtained by them after treatment with alcoholic potassium hydroxide must have consisted largely of benzyl ether.

When a mixture of benzyl isobutyrate and sodium benzyloxide is heated at 300—310° in a sealed tube, benzyl alcohol, benzyl ether, isobutyric acid, benzoic acid, and traces of benzaldehyde are obtained, but α -benzylisobutyric acid is not produced. It is probable that the substance described by Hodgkinson (Trans., 1878, 33, 495) as benzyl α -benzylisobutyrate consisted of benzyl ether. E. G.

Ketonic Decomposition of the Triphenylcarbinols. OTTO FISCHER and WALTER HESS (*Ber.*, 1905, 38, 335—339).—Trinitrotriphenylmethane is hardly affected by a boiling solution of chromic acid in acetic acid, but is decomposed when heated with nitric acid of sp. gr. 1.4 for 3 hours at 150°, giving 4 : 4'-dinitrobenzophenone; small quantities of this substance are also formed in the preparation of

trinitrophenylcarbinol by the oxidation of trinitrotriphenylmethane by the air in presence of alkali.

Tri-p-bromotriphenylmethane, $C_{19}H_{13}Br_3$, prepared from *p*-leucaniline by means of the diazo-reaction, crystallises from light petroleum in thick, colourless prisms and melts at 112° ; it is oxidised by chromic acid in acetic acid solution to a mixture of 20 per cent. of 4:4'-dibromobenzophenone and 80 per cent. of *tri-p-bromotriphenylcarbinol*, which crystallises from benzene or light petroleum in thick plates and melts at 133° .

Tri-p-chlorotriphenylmethane crystallises from light petroleum in prisms, melts at $87-88^\circ$, and on oxidation with chromic acid, as in the foregoing case, gives mostly *trichlorotriphenylcarbinol*, which separates from light petroleum containing benzene in thick crystals melting at 98° ; a little dichlorobenzophenone is formed.

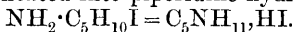
Tri-p-iodotriphenylmethane forms slightly yellow crystals, melts at $131-132^\circ$, and on oxidation with chromic acid gives principally *tri-p-iodotriphenylcarbinol*, although some 4:4'-di-iodobenzophenone is formed; the carbinol crystallises in long, yellow prisms and melts at 155° .

W. A. D.

ϵ -Halogen Derivatives of Amylamine. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1905, **38**, 169—179).—*Benzoyl- ϵ -phenoxyamylamide*, $NHBz \cdot [CH_2]_5 \cdot OPh$, prepared by warming an alcoholic solution of benzoyl- ϵ -chloroamylamide with phenol and sodium, separates from a mixture of ethyl alcohol and water in glistening leaflets and melts at 89° . When heated with three times its amount of hydrobromic acid, saturated at 0° , for 4 hours at 150° in a sealed tube, it formed ϵ -bromoamylamine hydrobromide, which was converted into the free base, $C_5H_{10}Br \cdot NH_2$, the *platinichloride* of which was analysed.

Benzoyl- ϵ -bromoamylamide, $NHBz \cdot C_5H_{10}Br$, forms snow-white crystals and melts at $59-61^\circ$.

When an alcoholic solution of benzoyl- ϵ -chloroamylamide is boiled with sodium iodide, *benzoyl- ϵ -iodoamylamide*, $NHBz \cdot C_5H_{10}I$, is formed; it crystallises in prisms and melts at $54-55^\circ$. ϵ -*Iodoamylamine*, prepared by heating its benzoyl derivative with fuming hydriodic acid in a sealed tube at 150° and then adding alkali, readily undergoes transformation when heated into piperidine hydriodide, thus:



Benzoyl- ϵ -iodoamylamide is more reactive than the corresponding bromo-compound. Whilst the latter reacts with difficulty with secondary bases, the former reacts with great readiness even at the ordinary temperature.

Benzoylpiperidylcadaverine, $NHBz \cdot [CH_2]_5 \cdot C_5NH_{10}$, formed by the action of benzoyl- ϵ -iodoamylamide on piperidine, separates from light petroleum in glistening crystals and melts at 74° . It dissolves readily in dilute acids; its *picrate* melts at 104° .

ϵ -*Benzoylamino-n-hexonitrile* (*benzoyl- ϵ -leucine nitrile*),
 $NHBz \cdot [CH_2]_5 \cdot CN$,

prepared by the action of benzoyl- ϵ -iodoamylamide on a solution of potassium cyanide in a mixture of water and alcohol, separates from

water or dilute alcohol in snow-white, glistening leaflets and melts at 95° . When hydrolysed, it forms ϵ -leucine, $\text{NH}_2 \cdot [\text{CH}_2]_5 \cdot \text{CO}_2\text{H}$, whilst by reduction and subsequent hydrolysis, hexamethylenediamine, $\text{NH}_2 \cdot [\text{CH}_2]_6 \cdot \text{NH}_2$, is produced.

By the action of phosphorus pentachloride on benzoylamino- ϵ -hexonitrile, the imide chloride, $\text{CPhCl} \cdot \text{N} \cdot [\text{CH}_2]_5 \cdot \text{CN}$, is formed, which, on elevation of temperature, is transformed into a mixture of benzonitrile and ϵ -chlorohexonitrile, $\text{C}_5\text{H}_{10}\text{Cl} \cdot \text{CN}$. When the latter compound is mixed with a solution of phenol and sodium in ethyl alcohol, ϵ -phenoxyhexonitrile, $\text{OPh} \cdot [\text{CH}_2]_5 \cdot \text{CN}$, is formed as snow-white crystals which melt at 36° .
A. McK.

Reaction between Organic Magnesium Compounds and Unsaturated Compounds. II. Reactions with Derivatives of Cinnamic Acid. ELMER P. KOHLER and GERTRUDE HERITAGE (*Amer. Chem. J.*, 1905, **33**, 21—35. Compare Abstr., 1904, i, 595).—When an ethereal solution of methyl cinnamate is added gradually to a solution of magnesium phenyl bromide at -10° and the resulting yellow magnesium compound is decomposed by shaking with finely-crushed ice, on dissolving the magnesium salts in hydrochloric acid at 0° , diphenylpropiophenone is produced together with *methyl $\beta\beta$ -diphenylpropionate*, which crystallises in large, lustrous prisms and melts at 47° ; a number of other substances are simultaneously formed. By the action of benzoyl chloride on the magnesium compound, benzoyl-triphenylpropenol is obtained together with a *benzoate*, $\text{C}_{23}\text{H}_{20}\text{O}_3$, which crystallises in long, white, silky needles, melts at 130 — 133° , and is easily hydrolysed with formation of benzoic acid and methyl diphenylpropionate. The relative amounts of diphenylpropiophenone and methyl $\beta\beta$ -diphenylpropionate produced vary with the temperature. At -10° , the quantity of the ketone obtained rarely exceeds 5 per cent. of the total product, whilst at 35° as much as 20 per cent. is formed. In the case of ethyl cinnamate, only a trace of ketone is produced at -10° , and less than 10 per cent. at 35° . The amyl ester yields only a trace of ketone at 35° and none at -10° .

By the action of magnesium methyl iodide on methyl cinnamate, dimethylstyrylcarbinol, $\text{CHPh} \cdot \text{CH} \cdot \text{CMe}_2 \cdot \text{OH}$, is produced, which, on oxidation with potassium permanganate, is converted into benzoic and hydroxyisobutyric acids. An oily *substance*, $\text{C}_{22}\text{H}_{26}\text{O}$, probably the ether, $\text{O}(\text{CMe}_2 \cdot \text{CH} \cdot \text{CHPh})_2$, amounting to less than 5 per cent. of the total product, is also formed, which boils at 128° under 11 mm. pressure, combines with bromine, and is oxidised by hot alkaline potassium permanganate; under certain conditions, benzylideneacetone is also produced.

By the action of magnesium phenyl bromide on cinnamyl chloride, diphenylpropiophenone, cinnamic acid, and $\beta\beta$ -diphenylpropionic acid are obtained, together with other compounds.

Cinnamylethylanilide, $\text{CHPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{NPhEt}$, obtained by the action of cinnamyl chloride on ethylaniline, crystallises in large, colourless prisms, melts at 74° , and is readily soluble in ether, alcohol, chloroform, or carbon disulphide and moderately so in boiling light petroleum. When this substance is treated with magnesium phenyl

bromide, $\beta\beta$ -diphenylpropionylethylanilide is produced, which is converted by bromine into *diphenylbromopropionylethylanilide*. This compound crystallises in large, colourless prisms, melts at 178° , is readily soluble in chloroform, acetone, or boiling alcohol, and is hydrolysed by hydrochloric acid with formation of α -bromo- $\beta\beta$ -diphenylpropionic acid, $\text{CHPh}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, which melts and decomposes at about 164° , is readily soluble in alcohol or ether, and when boiled with alcoholic potassium hydroxide is converted into β -phenylcinnamic acid. An attempt was made to prepare α -bromo- $\beta\beta$ -diphenylpropionic acid by the direct bromination of diphenylcinnamic acid, but it was found that the main product of the reaction was phenylhydrindone.

β -Phenylcinnamic acid, $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$, crystallises in colourless needles, melts at 142° , is readily soluble in alcohol or ether, and moderately so in boiling water, does not combine with bromine at the ordinary temperature, but is oxidised by cold potassium permanganate solution with formation of benzophenone and carbon dioxide.

E. G.

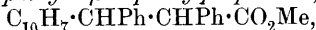
Reaction between Unsaturated Compounds and Organic Magnesium Compounds. IV. Reactions with Esters of α -Phenylcinnamic Acid. ELMER P. KOHLER and GERTRUDE HERITAGE (*Amer. Chem. J.*, 1905, 33, 153—163).—When an ethereal solution of methyl α -phenylcinnamate is treated with magnesium phenyl bromide, the compound $\text{CHPh}_2\cdot\text{CPh}\cdot\text{C}(\text{OMgBr})\cdot\text{OMe}$, is produced, which crystallises in small, lustrous prisms and if left for a day changes into a thick paste. By extracting this paste with chloroform, methyl $\alpha\beta\beta$ -triphenylpropionate, $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$, is obtained, which crystallises in hard, lustrous plates and melts at 159° . $\alpha\beta\beta$ -Triphenylpropionic acid crystallises in needles, melts at 211° , and is readily soluble in alcohol or ether, sparingly so in light petroleum, and insoluble in water. The ethyl ester crystallises in plates and melts at 120° .

When the additive compound of methyl α -phenylcinnamate with magnesium phenyl bromide is treated with dry hydrogen chloride, methyl triphenylpropionate and magnesium chloride are produced. It reacts with acetyl chloride with formation of the compound $\text{CHPh}_2\cdot\text{CPh}\cdot\text{C}(\text{OAc})\cdot\text{OMe}$, which crystallises from alcohol in plates, melts at 75° , and on hydrolysis yields acetic acid and methyl triphenylpropionate. By the action of bromine on the magnesium compound, methyl triphenylbromopropionate, $\text{CHPh}_2\cdot\text{CPhBr}\cdot\text{CO}_2\text{Me}$, is produced, which crystallises in large, colourless prisms, melts and decomposes at 150 — 152° , and is readily soluble in chloroform or hot acetone and slightly so in alcohol or ether. When this ester is boiled with alcoholic potassium hydroxide, it is converted into triphenylacrylic acid, melting at 213° .

When methyl α -phenylcinnamate is treated with magnesium *o*-tolyl bromide, an additive compound separates in colourless crystals which, on decomposition with water, yields methyl *o*-tolylidiphenylpropionate, $\text{C}_7\text{H}_7\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CO}_2\text{Me}$. This ester crystallises in hard, lustrous plates, melts at 150° , and on hydrolysis is converted into *o*-tolylidi-

phenylpropionic acid, which crystallises in long needles and melts at 190° .

By the action of magnesium α -naphthyl bromide on methyl α -phenylcinnamate, an additive compound is produced which, on decomposition, yields *methyl β -1-naphthyl- $\alpha\beta$ -diphenylpropionate*,



which crystallises in small, lustrous pyramids or prisms, melts at 170° , and is readily soluble in chloroform, ether, or light petroleum. Another *methyl ester* is simultaneously produced which crystallises in large, lustrous prisms, melts at 128° , and is more soluble in organic solvents than the isomeride melting at 170° . These esters are perhaps stereoisomeric, but as they furnish the same acid on hydrolysis it is not possible to prove that they represent two racemic modifications. *β -1-Naphthyl- $\alpha\beta$ -diphenylpropionic acid* crystallises in short, thick needles and melts at 171° .

When methyl α -phenylcinnamate is treated with magnesium methyl iodide, $\gamma\delta$ -*diphenyl- β -methyl- $\Delta\gamma$ -buten- β -ol*, $\text{CHPh}\cdot\text{CPh}\cdot\text{CMe}_2\cdot\text{OH}$, is produced, which crystallises in thin plates or long, flat needles, melts at 68° , is readily soluble in acetone or ether and fairly so in light petroleum, is oxidised by alkaline permanganate with formation of benzoic and acetic acids, and does not combine with bromine.

E. G.

Mechanism of the Synthesis of Salicylic Acid. CORNELIS A. LOBBY DE BRUYN and S. TIJMSMA (*Rec. trav. chim.*, 1904, 23, 385—393).—When sodium phenyl carbonate is heated, its tension of dissociation becomes equal to the atmosphere at 85° ; beyond this, it increases until the temperature reaches 100° and then diminishes, this being due to the reabsorption of carbon dioxide and the formation of salicylic acid. These observations indicate that sodium phenyl carbonate may be an intermediate product in the production of sodium salicylate by Schmitt's method (Abstr., 1885, 709 and 982), but that it does not play this rôle under the conditions prescribed by Kolbe. It is suggested that in Kolbe's process the sodium phenoxide is first converted into the corresponding *o*-carboxylic acid, $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and that this then undergoes isomeric transformation into sodium salicylate.

Sodium phenoxide o-carboxylic acid (o-sodoxybenzoic acid) may be obtained as a white, crystalline powder by heating sodium phenyl carbonate in closed tubes at 100° for four days. When mixed with sodium phenoxide and heated at 150° in closed tubes, it furnishes disodium salicylate and phenol, and when heated with methyl iodide it yields methyl salicylate, probably as the result of isomeric transformation of the anisole-*o*-carboxylic acid first formed, since the latter, when heated during one day at 150° in the presence of small quantities of *o*-sodoxybenzoic acid, is completely converted into methyl salicylate. It is probable that there is also no intermediate formation of carbonates in the preparation of carboxylic acids from phloroglucinol (Will, Abstr., 1885, 906) or resorcinol (Senhofer and Brunner, Abstr., 1881, 265), but this may occur with hydroxyquinoline (Schmitt and Engelmann, Abstr., 1887, 738; 1888, 66).

T. A. H.

Action of Organo-magnesium Compounds on Phthalic Anhydride. HUGO BAUER (*Ber.*, 1905, **38**, 240—241. Compare Abstr., 1904, 417).—*Phthalophenone*, $\text{C}_6\text{H}_4\langle\text{CPh}_2\text{CO}\rangle\text{O}$, melting at 115° , is formed by the interaction of magnesium phenyl bromide and phthalic anhydride along with small quantities of a compound melting at 146° , probably identical with Zincke's β -dibenzoylbenzene. Further, the crude reaction mixture, on the addition of dilute sulphuric acid, yields a viscid, yellow oil soluble in light petroleum with a green fluorescence; in time, the fluorescence disappears and phthalophenone crystallises out. *Dibenzylphthalide*, $\text{C}_6\text{H}_4\langle\text{C}(\text{C}_7\text{H}_7)\text{CO}\rangle\text{O}$, forms colourless needles melting at $203\text{--}204^\circ$. By the interaction of magnesium *p*-tolyl bromide and phthalic anhydride, a brown resin is formed from which a compound, possibly *o*-ditoluoylbenzene, melting at $189\text{--}190^\circ$, isomeric with ditolylphthalide, was isolated. E. F. A.

Ethylidenephthalide. ADOLF DAUBE (*Ber.*, 1905, **38**, 206—209).—The ethylidenephthalide was prepared by Gottlieb's method (Abstr., 1899, i, 511) and hydrolysed to propiophenone-*o*-carboxylic acid.

This acid readily reacts with hydroxylamine yielding the *anhydride* of *propiophenoneoxime-o-carboxylic acid*, $\text{C}_6\text{H}_4\langle\text{CEt:N}\text{CO-O}\rangle$, which crystallises from hot water in prisms melting at 119° .

Hydrazine converts the acid into 1-ethylphthalazone (Paul, Abstr., 1899, i, 776), which can be readily alkylated, yielding 1:3-diethylphthalazone, $\text{C}_6\text{H}_4\langle\text{CEt:N}\text{CO-NEt}\rangle$. This melts at $49\text{--}50^\circ$ and distils at 307° . Phosphorus oxychloride reacts with ethylphthalazone, yielding 4-chloro-1-ethylphthalazine, $\text{C}_6\text{H}_4\langle\text{CEt:N}\text{CCl=N}\rangle$, which crystallises from alcohol in needles melting at 93° . On reduction with tin and hydrochloric acid, it yields ethyldihydroisindole, $\text{C}_6\text{H}_4\langle\text{CHEt}\text{CH}_2\rangle\text{NH}$, which boils at $327\text{--}329^\circ$.

The chloro-compound readily reacts with sodium alkyl oxides. 4-Methoxy-1-ethylphthalazine melts at 49° , the ethoxy-compound at 53° , and the phenoxy-derivative at 89° .

Ethylphthalimidine, $\text{C}_6\text{H}_4\langle\text{CHEt}\text{CO}\rangle\text{NH}$, obtained by the reduction of ethylphthalazone with zinc and hydrochloric acid, forms colourless crystals melting at 105° and turning red on exposure to the air.

Ethylidenephthalide yields an additive product with nitric peroxide; when this is crystallised from glacial acetic acid, a small amount of nitroethylidenephthalide, $\text{NO}_2\cdot\text{CMe}\cdot\text{C}\langle\text{O}\text{C}_6\text{H}_4\rangle\text{CO}$, is obtained. It crystallises in yellow needles melting at 123° . J. J. S.

Tolynaphthalimides and Naphthynaphthalimides. GUIDO BARGELLINI (*Gazzetta*, 1904, **34**, ii, 454—459).—The author has prepared *o*-tolynaphthalimide by the interaction of naphthalic anhydride

and *o*-toluidine, and finds that it crystallises from acetic acid in yellow needles melting at 217—218°; Janbert (Abstr., 1895, i, 239) gave 214°.

m-Tolynaphthalimide, $C_{10}H_6 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot C_6H_4Me$, crystallises from alcohol in shining, yellow needles melting at 175—176° and dissolves readily in acetic acid, ethyl acetate, or chloroform and to a slight extent in ether, benzene, or carbon disulphide.

p-Tolynaphthalimide, $C_{19}H_{13}O_2N$, crystallises from acetic acid in small, yellow needles melting at 304—305° and dissolves readily in chloroform and slightly in alcohol, carbon disulphide, benzene, or ethyl acetate.

α -Naphthynaphthalimide, $C_{10}H_6 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot C_{10}H_7$, separates from acetic acid as a yellow, crystalline powder melting at 214—215°, and is very soluble in carbon disulphide, chloroform, or nitrobenzene, and slightly so in ether, light petroleum, ethyl acetate, acetone, benzene, or methyl, ethyl, or amyl alcohol.

β -Naphthynaphthalimide, $C_{22}H_{13}O_2N$, crystallises from acetic acid in yellow needles melting at 291—292° and dissolves readily in chloroform or nitrobenzene, less so in methyl, ethyl, or amyl alcohol, benzene, ethyl acetate or acetone, and to a slight extent in ether, carbon disulphide, or light petroleum.

T. H. P.

The Oxonium Nature of Santonin. EDGAR WEDEKIND and A. KOCH (*Ber.*, 1905, 38, 421—428).—Santonin and such of its derivatives as contain the carbonyl group intact behave as oxonium compounds, and yield salts with acids and double compounds with certain metallic haloids. Desmotroposantonin and other enolic derivatives have no basic properties.

Santonin nitrate, $C_{15}H_{18}O_3 \cdot HNO_3$, forms colourless crystals and decomposes at 145°; it is stable in dry air, but is decomposed quantitatively into its components by water (compare Andreocci, *Atti R. Accad. Lincei*, 1896, [v], 5, ii, 309).

Santonin antimony pentachloride, $2C_{15}H_{18}O_3 \cdot SbCl_5 \cdot HCl$, prepared by mixing the components slowly in glacial acetic acid solution, forms colourless needles and decomposes at 145°. It dissolves readily in most organic solvents; water and alcohols decompose it. The rotation in acetone solution is that due to the santonin present. The hydrogen chloride in the salt is produced by chlorination of a part of the santonin (compare following abstract). *Santonin acid antimony pentachloride* forms stable crystals and decomposes at 145°.

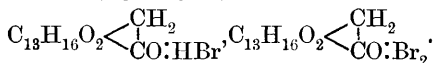
Santonin tin tetrabromide, $2C_{15}H_{18}O_3 \cdot SnBr_4 \cdot HBr$, forms yellow prisms and decomposes at 127°.

Oxonium salts of similarly abnormal composition have been described by Rosenheim and Levy (Abstr., 1904, i, 1024).

Santonin ferric chloride forms brown crystals and melts and decomposes at 210°; the bright yellow *platinichloride* is unstable. It was not found possible to prepare a hydrochloride, oxalate, or picrate; the ferro-, ferri-, and cobalti-cyanides will be described shortly.

C. H. D.

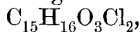
The Behaviour of Halogens towards Santonin. EDGAR WEDEKIND and A. KOCH (*Ber.*, 1905, 38, 429—435. Compare preceding abstract).—It was not found possible to prepare bromo-substituted derivatives of santonin as described by Klein (*Abstr.*, 1893, i, 112). Santonin reacts with bromine in acetic acid or chloroform solution to form a complex *oxonium bromide*, $C_{30}H_{37}O_6Br_3$, which contains two atoms of active bromine and one atom as hydrogen bromide, and thus has the constitution



It decomposes at 105° and slowly loses bromine under the action of light.

Santonin oxonium iodide, $C_{30}H_{37}O_6I_3$, forms dark olive-green tablets with metallic reflex, stable in dry air, and decomposes at 135° . It is less readily decomposed by water than the bromide.

The behaviour of chlorine is quite different from that of bromine, only substitution derivatives being formed. Dichlorosantonin,



prepared from santonin and dry chlorine in chloroform solution, forms long, colourless prisms, becomes yellow at 140° and decomposes at 175° . Chlorine water reacts with santonin, forming chlorosantonin, $C_{15}H_{17}O_3Cl$, which crystallises from dilute alcohol and melts and decomposes at 235° .

C. H. D.

Compounds from Lichen. WILHELM ZOPF (*Annalen*, 1905, 338, 35—70. Compare *Abstr.*, 1904, i, 1020).—Hesse's formula, $C_{28}H_{22}O_7$, for rhizocarpic acid is incorrect, the molecular formula being $(C_{13}H_{10}O_3)_2$.

Pseudovernia ericetorum contains atranoric acid, physodalin (Hesse's physodic acid), and a bitter material, but no furfuracic acid, isidic acid, or olivetoric acid. The *physodalin* forms crystals melting at 201 — 202° , and yields a *diacetyl* derivative melting at 158° . Hesse's lepraric acid could not be found in *Lepraria chlorina*.

Lepraria flava contains calycin, pinastric acid, and calyciarin. The last mentioned crystallises in rhombic plates and is insoluble in alkali hydroxides. *Lecanora varia* yields psoromic acid and *l*-usnic acid, the latter having $[\alpha]_D - 489.2^\circ$ in chloroform at 17° . *Catocarpus oreites* contains rhizocarpic acid and psoromic acid. *Usnea Schraderi* contains usnaric acid, *d*-usnic acid ($[\alpha]_D + 498.3^\circ$ in chloroform), and a colourless substance which could not be identified. Hesse's ochrolechiaic acid, obtained from *Ochrolechia pallescens* var. *parella*, is identical with variolaric acid; the former melts at about 280° , the latter at 283° . *Parmelia revoluta* yields atranoric acid and gryphoric acid. The latter acid is characterised by a very delicate blood-red coloration with bleaching powder. *Parmelia pilosella* yields atranoric acid and a crystalline bitter material, *pilosellic acid*; the latter melts at 245° and gives a violet coloration with ferric chloride and a yellow solution with potassium hydroxide and ammonia. From *Stictina gilva*, stictinin was isolated, which crystallises in needles melting at 160 — 161° , giving a reddish-violet coloration with ferric chloride and a cinnabar-red coloration with concentrated sulphuric acid, changing to an

orange-yellow solution with more acid. Rhizocarpic acid was found in *Calycium hyperellum*. K. J. P. O.

o-Methylaminobenzaldehyde. OTTO SCHMIDT (*Ber.*, 1905, 38, 200—203. Compare Heller, *Abstr.*, 1904, i, 160; Bamberger, *ibid.*, 422).—The physical constants of Heller's methylanthranil indicate that it cannot be a homologue of anthranil, but rather a mixture of methyl- and dimethyl-o-aminobenzaldehydes. Refractometric determinations have shown that the group N·C·C·CO always produces an abnormally high refraction in a compound.

	Sp. gr. at <i>t.</i>	<i>n</i> _D .	M _D .
o-Methylaminobenzaldehyde...	1·1092 11·8°/4°	1·62773	43·177
Methyl methylanthranilate ...	1·1348 12·3 /4	1·58395	48·658
Ethyl aminoacetate 1·0358 11·8 /4	1·42737	25·55
Acetylthranil 1·2034 73·3 /4	1·56862	43·81

(Compare Brühl, *Abstr.*, 1904, i, 92 and 160.)

J. J. S.

β-Hydroxynaphthaldehyde. MARIO BETTI and CURIO M. MUNDICI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 542—550).—β-Hydroxynaphthaldehydophenylhydrazone and β-hydroxynaphthylideneaniline have already been described (Gattermann and Horlacher, *Abstr.*, 1899, i, 372).

β-Hydroxynaphthylidene-p-nitroaniline, OH·C₁₀H₆·CH:N·C₆H₄·NO₂, crystallises from alcohol in dark red needles showing a metallic green reflex, or from benzene in yellowish-red scales or ruby-red plates melting at 222°.

1:2-Naphthacoumarincarboxylic acid, C₁₀H₆ < $\begin{matrix} \text{CH:C}\cdot\text{CO}_2\text{H} \\ \text{O—CO} \end{matrix}$, prepared

by the condensation of β-hydroxynaphthaldehyde and malonic acid in presence of acetic acid, crystallises from alcohol in scales or in yellow, silky needles melting and decomposing at 233°; the alcoholic solution exhibits vivid yellowish-blue fluorescence, and is faintly alkaline to litmus.

The action of dry hydrogen chloride on β-hydroxynaphthaldehyde in methyl alcoholic solution yields a *hydrochloride* of *dinaphthaxanthidrole*, CH < $\begin{matrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{matrix}$ > O·Cl, separating as a green, crystalline mass, which dissolves in acetic acid giving an intensely brown coloration, and is decomposed by water even in the cold; at 115°, it forms drops, and at 216—218° it melts and decomposes. When treated with methyl alcohol in the cold, it yields the corresponding *methyl* derivative, OMe·CH < $\begin{matrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{matrix}$ > O, which crystallises from methyl alcohol in pale yellow, strongly refracting prisms melting at 178°. Cold ethyl alcohol yields (1) the *ethyl* derivative, C₂₈H₁₈O₂, which crystallises from alcohol in colourless, silky needles melting at 149° and reddening slightly in the air; it has the normal molecular weight in freezing benzene, and forms a bright red *picate* melting at 241°; (2) *dinaphthaxanthene*, CH₂ < $\begin{matrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{matrix}$ > O, which is obtained in larger yield by

the action of hot ethyl alcohol on the hydrochloride, and crystallises from benzene in shining, colourless needles melting at 203—204°.

T. H. P.

The 3-Methyl-6-alkylcyclohexanones and the Corresponding Phenols, Homologues of Menthone and Menthol. ALBIN HALLER (*Compt. rend.*, 1905, 140, 127—130).—When the sodium derivative of 3-methylcyclohexanone, prepared by the action of sodamide on the ketone, is treated with an alkyl iodide, the corresponding 3-methyl-6-alkylcyclohexanone is obtained (compare Abstr., 1904, i, 600). By the prolonged action of methyl iodide on the sodium derivative of 3-methylcyclohexanone a mixture of the *di*-, *tri*-, *tetra*-, and *penta*-methylcyclohexanones is formed. 3-Methyl-6-ethylcyclohexanone, $C_9H_{16}O$, boils at 83—84° under 18 mm. pressure, has a sp. gr. 0.9016 at 15°/4° and $[\alpha]_D + 8.32'$, and yields a semicarbazone melting at 152—154°. 3-Methyl-6-propylcyclohexanone, $C_{10}H_{18}O$, boils at 97—98° under 18 mm. pressure, has a sp. gr. 0.8994 at 15°/4° and $[\alpha]_D + 3.21'$; its semicarbazone melts at 154—156°. 3-Methyl-6-allylcyclohexanone, $C_{10}H_{16}O$, boils at 98—99° under 18 mm. pressure, has a sp. gr. 0.9233 at 15°/4°, and $[\alpha]_D + 18.2'$; its semicarbazone melts at 146—148°. 3-Methyldiallylcyclohexanone, $C_{13}H_{20}O$, boils at 130—132° under 20 mm. pressure, has a sp. gr. 0.9365 at 15°/4°, and $[\alpha]_D + 62.2'$; its semicarbazone melts at 141—143°. 3-Methyl-6-isobutylcyclohexanone, $C_{11}H_{20}O$, boils at 93—95° under 11 mm. pressure, has a sp. gr. 0.9950 at 15°/4° and $[\alpha]_D + 0.24'$; its semicarbazone melts at 171—173°.

The 3-methyl-6-alkylcyclohexanones, on reduction with sodium in absolute alcohol, yield the corresponding phenols, which have an odour similar to that of menthol, boil at a slightly higher temperature than the ketone from which they are derived, and form condensation products with benzaldehyde which are oxidised by potassium permanganate to form the α -methyl- δ -alkyladipic acid and benzoic acid according to the equation $CH_2 < \begin{smallmatrix} CH_2 \cdot CHMe \\ CHR \cdot CO \end{smallmatrix} > C : CHPh + O = CO_2H \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CHR \cdot CO_2H + PhCO_2H$.

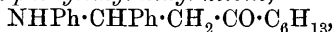
3-Methyl-6-ethylcyclohexanol, $C_9H_{18}O$, boils at 85—87° under 11 mm. pressure; 3-methyl-6-propylcyclohexanol, $C_{10}H_{20}O$, distils at 102—104° under 15 mm. pressure. 3-Methyl-6-allylcyclohexanol, $C_{10}H_{18}O$, boils at 98—100° under 10 mm. pressure. 3-Methyl-6-isobutylcyclohexanol, $C_{11}H_{22}O$, crystallises from light petroleum in thin needles melting at 68—69°; a liquid stereoisomeride boils at 110—112° under 16 mm. pressure.

M. A. W.

Condensation of Imines with Aldehydes and Ketones. CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], 33, 157—162. Compare Abstr., 1904, i, 832).—When molecular solutions of acetophenone and benzylideneaniline in alcohol are mixed, anilinobenzylacetophenone, $COPh \cdot CH_2 \cdot CHPh \cdot NHPh$, is formed (Tambor and Wildi, Abstr., 1898, i, 313); from this, by the action of sulphuric acid, benzylideneacetophenone is produced. With benzylidene *p*-toluidine, *p*-toluidinobenzylacetophenone, $COPh \cdot CH_2 \cdot CHPh \cdot NH \cdot C_6H_4Me$, is obtained; this separates

from alcohol in small, colourless needles and melts at 172° . *β -Naphthyl-aminobenzylacetophenone*, $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, obtained by the interaction of acetophenone and benzylidene- β -naphthylamine, dissolved in alcohol, in presence of sodium methoxide, crystallises from boiling benzene in small needles, melts at 199° , and is slightly soluble in cold alcohol, more so on warming.

β -Anilino- β -phenyldiethyl ketone, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COEt}$, obtained by the interaction of methyl ethyl ketone with benzylideneaniline, crystallises from alcohol in small, colourless needles, melts at 121° , and is slightly soluble in cold alcohol, more so on warming. The solution in sulphuric acid furnishes on addition of excess of water benzylidenemethyl ethyl ketone, $\text{CHPh}\cdot\text{CH}\cdot\text{COEt}$ (Harries and Müller, Abstr., 1902, i, 295), instead of the quinoline derivative expected (compare Simon and Conduché, Abstr., 1904, i, 521). *β -Anilino- β -phenylethyl propyl ketone*, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPr}^a$, forms small needles and melts at 88° . *β -Anilino- β -phenylethyl hexyl ketone*,



forms colourless needles, melts at 92 – 93° , and is converted by sulphuric acid into *benzylidenemethyl hexyl ketone*, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_{13}$, which forms colourless needles melting at 34° . *β -Anilino- β -phenylethyl heptyl ketone*, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_7\text{H}_{15}$, crystallises in needles, melts at 93 – 94° , is slightly soluble in alcohol, readily so in ether, and with sulphuric acid yields *benzylidenemethyl heptyl ketone*, which crystallises from light petroleum in needles and from methyl alcohol in scales, melts at 52° , and is soluble in ether. *β -Anilino- β -phenylethyl nonyl ketone* forms small needles, melts at 96° , and furnishes benzylidenemethyl nonyl ketone.

T. A. H.

Reactions between Organic Magnesium Compounds and Unsaturated Compounds. III. Reactions with Compounds containing Bromine. ELMER P. KOHLER and RUTH M. JOHNSTIN (*Amer. Chem. J.*, 1905, 33, 35–45. Compare Abstr., 1904, i, 595, and this vol., i, 207, 208).—When an ethereal solution of ethyl α -bromocinnamate is added gradually to a solution of magnesium phenyl bromide and the resulting yellow precipitate is decomposed with ice-water, bromodiphenylpropiophenone (Kohler, Abstr., 1904, i, 596) is produced, together with benzoic acid and β -phenylcinnamic acid.

By the action of magnesium methyl iodide on ethyl α -bromocinnamate, an oily product is obtained which does not contain an ester and is slowly decomposed by boiling alcoholic potassium hydroxide with formation of potassium bromide, potassium benzoate, and a gum. When the oil is oxidised with dilute potassium permanganate, acetone, benzoic acid, and probably hydroxyisobutyric acid are obtained, whence it is concluded that the chief product of the reaction is a tertiary alcohol, $\text{CHPh}\cdot\text{CBr}\cdot\text{CMe}_2\cdot\text{OH}$.

When α -bromobenzylideneacetophenone is treated with magnesium phenyl bromide and the product decomposed with ice-water, a nearly theoretical yield of α -bromo- $\beta\beta$ -diphenylpropiophenone is produced. *Phenylbenzylideneacetophenone*, $\text{CPh}_2\cdot\text{CH}\cdot\text{COPh}$, obtained by the action of boiling alcoholic potassium hydroxide on bromodiphenylpropiophenone, crystallises in large, lemon-yellow prisms, melts at 92° , is

readily soluble in alcohol or ether and slightly so in light petroleum, and on oxidation with dilute potassium permanganate is converted into benzophenone and benzoic acid.

By the action of magnesium phenyl bromide on stilbene bromide, diphenyl is produced. Magnesium phenyl bromide reacts with ethyl dibromophenylpropionate with formation of diphenylpropiophenone and ethyl diphenylpropionate.

When benzylideneacetophenone bromide is slowly added to a solution of magnesium phenyl bromide at a low temperature, bromodiphenylpropiophenone and diphenylpropiophenone are produced, but if the reaction is carried out at 35° the products consist of diphenyl and diphenylpropiophenone.

By the action of magnesium naphthyl bromide on benzylideneacetophenone bromide, *naphthylphenylpropiophenone* is obtained, which crystallises in needles, melts at 121°, and is readily soluble in ether or alcohol.

When α -bromodiphenylpropiophenone is treated with an ethereal solution of magnesium phenyl bromide, diphenylpropiophenone and diphenyl are produced. If, however, the mixture is treated with benzoyl chloride before the addition of water, benzoyltriphenylpropenol is obtained.

E. G.

Pinacone-Pinacolin Rearrangement. SALOMON F. ACREE (*Amer. Chem. J.*, 1905, **33**, 180—195. Compare Abstr., 1904, i, 742, 747).—When dihydroxydiphenyldihydrophenanthrene is heated with acetyl

chloride, diphenylphenanthrone, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \end{array}$, is produced, which melts at 198° and is not easily oxidised by chromic acid (compare Werner and Grob, Abstr., 1904, i, 865). When this substance is heated with alcoholic potassium hydroxide at 150—190° for 6 hours, an *acid*, probably $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, is formed which melts at 180—190°.

By the action of magnesium phenyl bromide on acenaphthenequinone, *dihydroxydiphenyldihydroacenaphthene*, $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CPh} \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot \text{OH} \end{array}$, is obtained, which crystallises from alcohol or glacial acetic acid, melts at 154°, and when heated with acetyl chloride remains unchanged.

When *s*-diphenyldi-*p*-tolylpinacone (Acree, Abstr., 1904, i, 743) is heated with acetyl chloride for 10 hours, a *substance* is produced which is probably identical with the β -di-*p*-tolylidiphenylpinacolin described by Thörner and Zincke (Abstr., 1878, i, 223).

By the action of magnesium phenyl bromide on ethyl oxalate, β -benzopinacolin is not produced, but benzopinacone only is obtained (compare Dilthey and Last, Abstr., 1904, i, 667).

Tetraphenyltetramethylene glycol (Dilthey and Last, *loc. cit.*) melts at 206°. When ethyl succinate is treated with a boiling ethereal solution of magnesium phenyl bromide, a *substance*, probably tetraphenyltetramethylene oxide, $\begin{array}{c} \text{CH}_2 \cdot \text{CPh}_2 \\ | \\ \text{CH}_2 \cdot \text{CPh}_2 \end{array} \text{O}$, is formed, which crystallises from alcohol, melts at 163—165°, and slowly decolorises solution of bromine.

By the action of magnesium ethyl iodide on benzoïn, $\alpha\beta$ -diphenyl-butylene $\alpha\beta$ -glycol, $\text{OH}\cdot\text{CPhEt}\cdot\text{CHPh}\cdot\text{OH}$, is produced, which melts at $115-116^\circ$ and is only very slowly attacked by bromine.

Diphenyl-*m*-tolylcarbinol (Bistrzycki and Gyr, Abstr., 1904, i, 498) boils at 255° under 26 mm. pressure and melts at 65° . E. G.

Behaviour of Tetrabromo-*o*-benzoquinone towards Ketones and Aldehydes. C. LORING JACKSON and F. W. RUSSE (*Ber.*, 1905, 38, 419—421. Compare Abstr., 1904, i, 254).—Tetrabromo-*o*-benzoquinone does not combine with ketones and aldehydes to form compounds similar to those obtained from alcohols, but is converted by them into a mixture of hexabromo-*o*-quinocatechol ether,

$\text{C}_6\text{Br}_4\text{O}_2\cdot\text{C}_6\text{Br}_2\text{O}_2$, hexabromodihydroxycatechol ether, $\text{C}_6\text{Br}_4\text{O}_2\cdot\text{C}_6\text{Br}_2(\text{OH})_2$, and *hepta-bromo-*o*-quinocatechol hemiether*, $\text{OH}\cdot\text{C}_6\text{Br}_4\text{O}\cdot\text{C}_6\text{Br}_3\text{O}_2\cdot\frac{1}{2}\text{C}_6\text{H}_6$. The last compound crystallises from benzene in large, flat, yellow prisms, which lose benzene on exposure to air. It dissolves in ether, chloroform or nitrobenzene without decomposition; the alcoholic solution decomposes on warming and deposits hexabromo-*o*-quinocatechol ether. The hexabromo-compound is best prepared from tetrabromo-*o*-benzoquinone and acetone in the presence of benzene at the ordinary temperature, the reaction being completed in two weeks. When an excess of acetone is employed and the benzene is omitted, the two first-named compounds are chiefly obtained. Some bromoacetone is also produced, and when acetophenone is employed ω -bromoacetophenone is obtained.

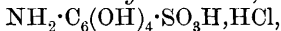
C. H. D.

Action of Potassium Iodide on Bromanil and Chloranil.

HENRY A. TORREY and W. H. HUNTER (*Ber.*, 1905, 38, 555—556).—When heated with potassium iodide in acetone solution, bromanil forms *dibromodi-iodo-*p*-benzoquinone*, $\text{C}_6\text{O}_2\text{Br}_2\text{I}_2$, which crystallises in reddish-brown prisms or golden plates, commences to sublime at about 240° , melts at about 255° , is easily soluble in benzene, toluene, hot acetone, or ethyl acetate, but only slightly so in alcohol, ether, or light petroleum; it dissolves in hot aqueous sodium hydroxide to a purple solution, and is easily reduced to the colourless *quinol*. With sodium phenoxide in aqueous solution, the quinone forms a *phenoxy*-derivative, with diphenylamine, in light petroleum solution, an *additive* compound, $\text{C}_6\text{O}_2\text{Br}_2\text{I}_2\cdot\text{NHPh}_2$, which separates in dark red crystals, and with *o*-toluidine a similar *additive* compound. The action of powdered potassium iodide on chloranil, partly dissolved in acetone, leads to the formation of a green *substance*, which contains potassium, and when treated with water yields a yellow, insoluble *compound* and a purple solution. Under the same conditions, bromanil yields a similar derivative. G. Y.

2-Nitro-3 : 6-dihydroxy-*p*-benzoquinone-5-sulphonic Acid. RUDOLF NIETZKI and ALFRED HUMANN (*Ber.*, 1905, 38, 453—454).—Potassium 3 : 6-dichloroquinol-2 : 5-disulphonate, prepared by the

action of potassium sulphite on chloranil, reacts on warming with potassium nitrite to form *potassium 2-nitro-3:6-dihydroxy-p-benzoquinone-5-sulphonate*, $\text{NO}_2 \cdot \text{C}_6\text{O}_2(\text{OK})_2 \cdot \text{SO}_3\text{K}$, which crystallises from water in yellow needles. The acid may be regarded as nitranilic acid in which one nitro-group is replaced by a sulpho-group. Silver nitrate precipitates a yellow, crystalline *potassium silver salt*, $\text{C}_6\text{O}_9\text{NSKAg}_2$. Stannous chloride reduces the potassium salt, yielding *2-amino-3:6-dihydroxyquinol-5-sulphonic acid hydrochloride*,



which forms colourless crystals, becoming brown on exposure to air. It was not found possible to break down the ring by oxidation.

C. H. D.

Dissociation of Phenoquinone and Quinhydrone. HENRY A. TORREY and H. HARDENBERGH (*Amer. Chem. J.*, 1905, **33**, 167—179. Compare Biltris, *Abstr.*, 1899, i, 199).—As a preliminary to the study of the dissociation of phenoquinone, the molecular weights in benzene solution of its dissociation products, phenol and quinone, were determined. Determinations of the molecular weight of phenol by the ebullioscopic method gave results which show that this substance is somewhat polymerised at the boiling point of benzene, and determinations by the cryoscopic method confirmed the conclusions of Beckmann (*Abstr.*, 1889, 11), Auwers (*Abstr.*, 1894, ii, 133), and others that phenol is polymerised even at low concentrations, and that the polymerisation increases with the concentration. The average value obtained for the molecular weight of quinone by the boiling point method was 116, and by the freezing point method 105. The results of the cryoscopic determinations agree with those obtained by Auwers (*loc. cit.*), and show that the molecular weight of quinone is not affected by the concentration.

Determinations of the molecular weight of phenoquinone by both methods have shown that this substance is highly dissociated in benzene solution; Biltris (*loc. cit.*) has found that this is also the case in ethereal solution. When phenol is added to a saturated solution of phenoquinone, a considerable quantity of phenoquinone separates, showing that phenol and quinone are the dissociation products. The action of these dissociation products on dissolved phenoquinone was studied by both ebullioscopic and cryoscopic methods. The results of these experiments are tabulated, and show that by the addition of one of the dissociation products to the dissociated phenoquinone solution a re-association takes place.

A determination of the molecular weight of quinhydrone in benzene solution has shown that the substance is completely dissociated into quinone and quinol, as Biltris (*loc. cit.*) has shown is the case in ethereal solution. If quinhydrone is dissolved in warm chloroform and the solution is slowly cooled, quinol separates at about 35°. As in the case of phenoquinone, quinhydrone may be precipitated from its solution by the addition of one of its dissociation products.

The yellow colour of solutions of phenoquinone and quinhydrone in various organic solvents shows that, in general, both substances are dissociated.

E. G.

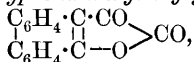
vic-m-Xylenol and Tetramethyldiphenoquinone. KARL AUWERS and TH. VON MARKOVITS (*Ber.*, 1905, 38, 226—237).—3 : 5 : 3' : 5'-Tetramethyldiphenoquinone-4 : 4', $C_{12}H_4Me_4O_2$, is best prepared by oxidising *vic-m*-xylenol dissolved in glacial acetic acid with chromic anhydride. Within 15—20 minutes, the quinone separates in glistening needles; crystallised from nitrobenzene or xylene, it separates in dark red needles and melts when fairly quickly heated at 210° . The quinone is also obtained when other oxidising agents are employed, as, for example, ferric salts, but the chromic anhydride method gives the best results. Hydroxylamine and phenylhydrazine act as reducing agents; the quinone is best reduced by the action of zinc-dust on the suspension in boiling acetic acid. The quinol, 3 : 5 : 3' : 5'-tetramethyl-4 : 4'-diphenol, $C_{12}H_4Me_4(OH)_2$, so obtained, crystallises in colourless glass, glistening needles and flat prisms melting at 220 — 221° ; the *diacetate* separates from acetic acid in long needles melting at 174 — 175° . The diphenol is very easily reoxidised to the quinone, especially in alkaline solution, a *quinhydrone* being formed as an intermediate product; this crystallises in dark steel-blue plates melting at 201° . 2-Chloro-3 : 5 : 3' : 5'-tetramethyl-4 : 4'-dihydroxydiphenyl, $OH \cdot C_6H_3ClMe_2 \cdot C_6H_2Me_2 \cdot OH$, prepared by the action of concentrated hydrochloric acid on the quinone, crystallises in needles melting at 203° .

It is shown that only those phenols in which both the ortho-positions relative to the hydroxyl group are occupied and both the meta- and para-positions are free undergo easy oxidation to diphenoquinone derivatives in this manner. Further, the analogy between tetramethyldiphenoquinone and coerulignone (tetramethoxydiphenoquinone) is pointed out (compare Liebermann, *Abstr.*, 1873, 1033; Hofmann, *Abstr.*, 1878, 417, and Herzig and Pollak, *Abstr.*, 1904, i, 808, 876).
E. F. A.

Alizarin Dimethyl Ether. CARL GRAEBE (*Ber.*, 1905, 38, 152—153. Compare *Abstr.*, 1902, i, 42).—The action of methyl sulphate on deoxyalizarin in alkaline solution leads to the formation of the *dimethyl ether*, $C_6H_4 \begin{array}{c} \text{CH}_2 \cdot \text{C} : \text{C}(\text{OMe}) \cdot \text{C} \cdot \text{OMe} \\ \text{CO} - \text{C} : \text{CH} - \text{CH} \end{array}$, which crystallises in golden needles, melts at 150° , is easily soluble in alcohol, dissolves in concentrated sulphuric acid to a reddish-yellow solution, and is oxidised by sodium chromate and glacial acetic acid to *alizarin dimethyl ether*, $C_{16}H_{12}O_4$. This crystallises in golden needles, melts at 215° , is easily soluble in benzene or chloroform, and moderately so in hot alcohol, and dissolves in concentrated sulphuric acid to a red solution. It is identical with the dimethyl ether obtained from 1-nitro-2-methoxyanthraquinone (Farbwerke vorm. Meister, Lucius, & Brüning).
G. Y.

Action of Alcoholic Potassium Hydroxide on Phenanthraquinone. RICHARD MEYER and OSKAR SPENGLER (*Ber.*, 1905, 38, 440—450).—In the preparation of diphenic acid by the action of alcoholic potassium hydroxide on phenanthraquinone, a yellow sub-

stance is first obtained, and is converted into diphenic acid by prolonged boiling. The alcohol takes part in the reaction, the yellow compound not being obtained in aqueous or methyl alcoholic solution. The same compound is obtained by heating phenanthraquinone and glycollic acid in methyl alcoholic solution, $C_{14}H_8O_2 + C_2H_4O_3 = C_{16}H_8O_3 + 2H_2O$. It is the *lactone* of 10-hydroxyphenanthryl-9-glyoxylic acid,



which crystallises from organic solvents in orange needles and melts and decomposes at $220-221^\circ$. It dissolves in alkalis to yellow solutions, from which it is reprecipitated by acids. The *barium* salt, $C_{16}H_8O_4Ba$, forms pale yellow, felted needles. The *phenylhydrazone* forms reddish-yellow needles and melts and decomposes at 254° .

Zinc dust reduces the lactone in alkaline solution to *diphenylene-dihydrofuran*, $\begin{array}{c} C_6H_4 \cdot C \cdot CH_2 \\ | \\ C_6H_4 \cdot C - O \end{array} > CH_2$, which crystallises from dilute acetic acid in long, flat needles and melts at 152° .

When fused, the lactone evolves carbon monoxide and carbon dioxide, forming a mixture of the compounds $\begin{array}{c} C_6H_4 \cdot C \cdot CO \cdot C \cdot C_6H_4 \\ | \quad | \\ C_6H_4 \cdot C \cdot CO \cdot C \cdot C_6H_4 \end{array}$ and $\begin{array}{c} C_6H_4 \cdot C \cdot CO \cdot C \cdot C_6H_4 \\ | \quad | \\ C_6H_4 \cdot C - O - C \cdot C_6H_4 \end{array}$. C. H. D.

A Synthesis of Menthone and Menthol. ALBIN HALLER and CAMILLE MARTINE (*Compt. rend.*, 1905, 140, 130—132).—3-Methyl-6-isopropylcyclohexanone, prepared by the action of isopropyl iodide on the sodium derivative of optically active 3-methylcyclohexanone (this vol., i, 214), boils at $207-209^\circ$, has a sp. gr. 0.9008 to 0.9017 at 17° , and $[a]_D + 12.56'$ to $8.52'$, and is a mixture of *d*- and *l*-menthone yielding an oxime, a semicarbazone, and a condensation product with benzaldehyde, which are respectively identical with the corresponding derivatives of menthone; on reduction with sodium in absolute alcohol, it is converted into menthol, m. p. $42-43^\circ$, which combines with phthalic acid to form a menthyl hydrogen phthalate melting at 120° .

M. A. W.

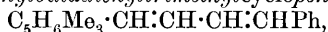
Cinnamylidenecamphor and its Reduction Products. HANS RUPE and GUNNAR FRISSELL (*Ber.*, 1905, 38, 104—122).—Cinnamyl-

idenecamphor, $C_8H_{14} \begin{array}{c} CO \\ \diagup \quad \diagdown \\ C : CH : CH : CHPh \end{array}$ was described by Haller (Abstr., 1891, 1498) as an uncrystallisable oil, but when prepared from sodium camphor and cinnamaldehyde in toluene suspension it may be obtained in a solid form, and then crystallises from alcohol in yellow, amber-like, rhombic crystals, $[a:b:c = 0.84856 : 1 : 1.8632]$ insoluble in water, dissolving readily in ether, benzene, or chloroform. It melts at $88-89^\circ$ and boils at $227-228.5^\circ$ under 11 mm. pressure and at 159° in the vacuum of the cathode light; $[a]_D$ was found to be $+269.74^\circ$ in benzene and $+296.11^\circ$ in chloroform.

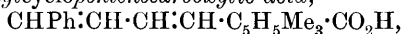
Sodium amalgam reduces cinnamylidenecamphor in methyl alcoholic

solution to γ -phenylpropylcamphor, $C_8H_{14} \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CH \\ | \end{smallmatrix} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot Ph$, boiling at 200° under 11 mm. pressure and dissolving readily in organic solvents. It has a sp. gr. 1.0064 at $20^\circ/4^\circ$; n_D 1.5242; $[\alpha]_D + 66.53^\circ$ in chloroform. Potassium permanganate oxidises it to benzoic and camphoric acids. It does not yield additive products with bromine or hydrogen bromide.

On heating cinnamylidenecamphor with a cold saturated solution of hydrogen bromide in glacial acetic acid at 100° , an oily product is obtained, consisting of a mixture of a bromo-acid and a brominated hydrocarbon. Zinc dust and acetic acid reduce it. The reduction product contains phenylbutadienyltrimethylcyclopentane,

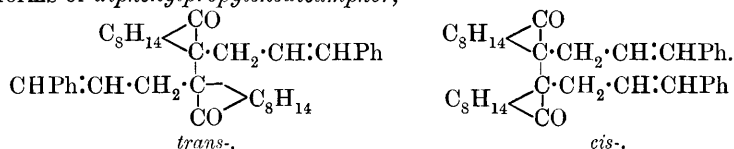


a colourless, uncrystallisable oil boiling at 180° under 10 mm. pressure, and having a sp. gr. 0.9995 at $20^\circ/4^\circ$, n_D 1.54089, and $[\alpha]_D + 3.86^\circ$. The second reduction product is phenylbutenyl- or phenylbutadienyl-trimethylcyclopentenecarboxylic acid,



which boils at $236-238^\circ$ under 12 mm. pressure and has a sp. gr. 1.0007 at $20^\circ/4^\circ$ and n_D 1.52901.

Zinc dust and acetic acid reduce cinnamylidenecamphor, and the product may be separated by crystallisation from alcohol, followed by fractional distillation of the uncrystallisable portion into four fractions, the first two of which yield on crystallisation geometrically isomeric forms of diphenylpropylenedicamphor,



The *trans*-modification crystallises from alcohol in white leaflets, melts at 188° , dissolves readily in ether, benzene or chloroform, and has $[\alpha]_D + 40.63^\circ$. The *cis*-modification crystallises in microscopic leaflets, melts at 152° , dissolves readily in organic solvents, and has $[\alpha]_D + 30.22^\circ$. Both forms react with bromine in chloroform solution to form a dibromo-derivative, $C_{38}H_{44}O_2Br_2$, a yellow, crystalline powder melting at 118° , which yields the *trans*-compound on reduction. Both the *cis*- and *trans*-compounds combine with hydrogen bromide in glacial acetic acid solution, yielding a mixture of an α -hydrobromide, $C_{38}H_{48}O_2Br_2$, melting at 168° , and a β -hydrobromide melting at 215° and dissolving more readily in organic solvents than the α -isomeride.

Zinc dust and acetic acid reduce the α -hydrobromide to *trans*-di- γ -phenylpropyldicamphor, $C_{38}H_{50}O_2$, which crystallises from alcohol in small cubes and melts at 162° . In similar manner, the β -hydrobromide yields on reduction *cis*-di- γ -phenylpropyldicamphor, which separates from alcohol as a white, crystalline powder and melts at 205° . Both isomerides are stable towards potassium permanganate, bromine, and hydrogen bromide.

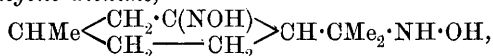
The third fraction from the reduction of cinnamylidenecamphor is

an uncrystallisable oil. The last fraction contains a *compound*, $C_{38}H_{46}O_8$, which crystallises from alcohol in white, silky needles and melts at 250° .
C. H. D.

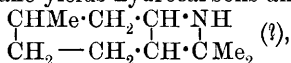
Transformation of Carvone and Eucarvone into Carvacrol and the Velocity of this Transformation. T. M. M. DORMAAR (*Rec. trav. chim.*, 1904, **23**, 394—400).—The measurements were made by heating solutions of the ketones in acetic acid with phosphoric oxide at 205° and observing the changes in specific gravity which took place. In the case of carvone, an attempt was made to use the change of specific rotation as a criterion of the progress of transformation, but this method was abandoned owing to the production of a small amount of colouring matter which interfered with the accuracy of the readings.

The reaction in both cases was unimolecular; the mean value of k in the case of the carvone transformation was 0.038, and for that of eucarvone 0.019.
T. A. H.

Oximes of Pulegone. FRIEDRICH W. SEMMLER (*Ber.*, 1905, **38**, 146—148. Compare Beckmann and Pleissner, *Abstr.*, 1891, 936; Wallach, *Abstr.*, 1896, i, 309; Harries and Roeder, *Abstr.*, 1900, i, 182).—*Pulegone dioxime*,



is obtained when the alcoholic-etheral solution of the product of the action of hydroxylamine, according to Beckmann's method, on pulegone is extracted with a small quantity of concentrated aqueous sodium hydroxide and carbon dioxide passed through the alkaline extract. It melts at 118° and is reduced, by sodium and alcohol, to 3:8-diamino-menthane, $CHMe \begin{array}{c} \text{CH}_2 \cdot C(NH_2) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} > CH \cdot CMe_2 \cdot NH_2$, which boils at $118\text{--}121^\circ$ under 10 mm. pressure and has a sp. gr. 0.956 at 20° , and n_D 1.489; the thiocarbamide derivative, $C_{21}H_{32}N_4S_2$, melts at 157° . The action of nitrous acid on the sulphate of the base in aqueous solution leads to the formation of the *glycol*, $C_{10}H_{20}O_2$, which boils at $146\text{--}148^\circ$ under 10 mm. pressure and is converted by the action of dilute sulphuric acid into *isopulegol*. When distilled, the hydrochloride of 3:8-diaminomenthane yields hydrocarbons and a *base*,



which boils at 65° under 15 mm. pressure and forms an insoluble *picrate* melting at 130° .
G. Y.

Camphene, Camphenylone, isoborneol, and Camphor. LOUIS BOUVEAULT and GUSTAVE BLANC (*Compt. rend.*, 1905, **140**, 93—95).—Methylcamphenylol, obtained by Wagner, Moycho, and Zienkowski by the action of magnesium methyl iodide on camphenylone (*Abstr.*, 1904, i, 438), behaves as a tertiary alcohol on boiling with pyruvic acid (compare Bouveault, *Abstr.*, 1904, i, 465), the main product of the reaction being camphene, which reacts with the pyruvic acid to form *isobornyl pyruvate*, boiling at $133\text{--}134^\circ$ under 11 mm. pressure, and yielding a

semicarbazone melting at 214° or 221° according to the rate of heating. *iso*Borneol, on the contrary, behaves as a primary or secondary alcohol when heated with pyruvic acid, forming a pyruvate the semicarbazone of which is identical with the one already described. M. A. W.

Green Colour of Kajeput Oil. H. C. PRINSEN GEERLIGS (*Chem. Centr.*, 1905, 1, 95; from *Chem. Weekblad*, 1904, 1, 931—934).—The green colour of the oil is due to the presence of copper, this being dissolved by the butyric and valeric acids and the esters of these which are contained in the oil. This was shown by experiments with the purified oil from which the acids and esters had been completely removed. This purified oil, after addition of water and either ethyl formate, acetate, propionate, butyrate, valerate, lactate, citrate, oxalate or cinnamate and a small quantity of the corresponding acid, was treated with copper shavings. The butyrate and valerate mixtures were the only ones which developed a green colour, the copper dissolving in the aqueous layer in all the other cases.

Valerian oil also dissolves copper, and, as in the case of kajeput oil, the green colour cannot be removed by shaking out with water.

H. M. D.

Peppermint Oil from Java. P. VAN DER WIELEN (*Chem. Centr.*, 1905, 1, 95; from *Pharm. Weekblad*, 1904, 41, 1081—1084).—Examination of an essential oil obtained from *Mentha javanica* gave the following data. It was light green in colour, had a bitter taste and an odour resembling peppermint. Sp. gr. = 0.9214 at 15° ; $\alpha_D + 4^{\circ}40'$ at 20° in a 100 mm. tube. It dissolved in one and a half times its volume of 70 per cent. alcohol. After cooling to -60° , it became entirely liquid again at -15° . It contained a considerable amount of pulegone, but little or no menthol or menthone.

H. M. D.

Varieties of Caoutchouc. Weber's Dinitrocaoutchouc. CARL D. HARRIES (*Ber.*, 1905, 38, 87—90. Compare Abstr., 1902, i, 811; 1903, i, 189, 642; 1904, i, 757, 1038; Weber, Abstr., 1902, i, 552; 1903, ii, 762).—The properties of Weber's compound of caoutchouc with nitric peroxide vary with the time during which the reagent is allowed to act. When rapidly prepared in benzene solution, the product is a yellow, sandy powder, decomposing at about 90° , insoluble in benzene, alcohol, ethyl acetate, chloroform, or carbon disulphide, but dissolving in nitrobenzene, aniline, pyridine, or quinoline on warming. When the product is allowed to remain 20 hours before filtering, it becomes soluble in ethyl acetate or acetone and decomposes at 157 — 160° . Its properties resemble those of Weber's compound, but the composition differs from the formula $C_{10}H_{16}O_4N_2$, assigned by him, and approaches that of the author's nitrosite, $C_{10}H_{15}O_7N_3$.

C. H. D.

Caoutchouc Nitrosite and its Use for the Analysis of Crude Caoutchoucs and Caoutchouc Products. I. PAUL ALEXANDER (*Ber.*, 1905, 38, 181—184).—According to Weber (Abstr., 1902, i, 552), a compound $C_{10}H_{16}O_4N_2$ is formed when a mixture of

nitrogen peroxide and oxygen is passed into caoutchouc solutions. The author, in amplification of earlier work (compare Abstr., 1904, i, 905), has now examined a considerable number of samples of caoutchouc from various sources according to Weber's method, but the products obtained did not possess the composition $C_{10}H_{16}O_4N_2$.

The figures for the analyses made agreed better for those of Harries' nitrosite "c" than for Weber's compound. A. McK.

African Copals. CH. COFFIGNIER (*Bull. Soc. chim.*, 1905, [iii], 33, 169—176).—Three West African resins known commercially as Kissel, Cameroon, and Accra copals are described. Kissel copal melts at 110° , has a sp. gr. 1.066 at 27° , acid number 70.4, Köttstorfer number 117.8, and is soluble in excess of boiling alcohol to the extent of 50 per cent.

Cameroon copal melts at 150° , has a sp. gr. 1.052 at 27° , acid number 159.7, Köttstorfer number 70.0, and is soluble to the extent of 45 per cent. in excess of boiling alcohol.

Accra copal melts at 120° , has a sp. gr. 1.033 at 27° , acid number 97.8, Köttstorfer number 140, and is soluble in excess of boiling alcohol to the extent of 90 per cent. The solubilities of the three copals in twelve different solvents are tabulated in the original.

T. A. H.

Decomposition Products of a Derivative of Artemisin (1:4-Dimethyl- β -naphthol and Propionic Acid). PASQUALE BERTOLO (*Gazzetta*, 1904, 34, ii, 322—326. Compare Abstr., 1902, i, 814, and 1904, i, 177).—When fused with potassium hydroxide, the product of the reduction of artemisin by stannous chloride and hydrochloric acid yields 1:4-dimethyl- β -naphthol (*loc. cit.*) and propionic acid. It hence behaves quite like the desmotroposantonins, but does not, like the latter, yield santonous acids on reduction with zinc dust and acetic acid. When, however, this reduction product of artemisin is subjected to reduction by Ladenburg's method, it yields a substance which is probably the corresponding acid, and is to be further investigated. Artemisin hence contains the same fundamental nucleus as santonin united to a propionic acid residue.

T. H. P.

[Theory of Dyeing.] WILHELM BILTZ (*Ber.*, 1905, 38, 184—187).—Polemical. A reply to Zacharias (this vol., i, 75). A. McK.

Researches in the Furan Series. R. MARQUIS (*Ann. Chim. Phys.*, 1905, [viii], 4, 196—288).—The paper is mainly a résumé of work already published (compare Abstr., 1900, i, 798; 1901, i, 222; 1902, i, 302, 483; 1903, i, 49, 370, 644; 1904, i, 82). The aldehyde obtained by the action of water on nitrosuccinaldehyde monoacetic (Abstr., 1902, i, 483) has been identified as maleic dialdehyde, and the following derivatives prepared: (1) a *diphenylhydrazone*, melting at 236 — 237° , by Maquenne's metallic block method, and yielding, on oxidation, the *tetrazone*, $\begin{array}{c} \text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{NPh} \\ || \quad || \\ \text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{NPh} \end{array}$, crystallising in scales of a magnificent red colour with a green reflex and melting at 174 — 175° ;

(2) the *dioxime*, $\begin{array}{c} \text{CH}\cdot\text{CH}\cdot\text{NOH} \\ | \\ \text{CH}\cdot\text{CH}\cdot\text{NOH} \end{array}$, decomposing at 220° and yielding a *dibenzoyl* derivative melting at 165° . M. A. W.

Beckmann's Rearrangement in Oximes of Ketone-alcohols of the Benzoin Type. ALFRED WERNER and TH. DETSCHEFF (*Ber.*, 1905, **38**, 69—84. Compare Werner and Piguet, this vol., i, 66).—In the preparation of α -benzoinoxime by Goldschmid and Polanovska's method (*Abstr.*, 1887, 492), the β -oxime is simultaneously produced, and a method for the separation of the oximes is described.

Acetyl- α -benzoinoxime, $\text{OAc}\cdot\text{N}:\text{CPh}\cdot\text{CHPh}\cdot\text{OH}$, separates from warm alcohol in colourless, granular crystals and melts at 112° . *Acetyl- β -benzoinoxime* forms long, flat prisms and melts at 111° . Chromic acid oxidises the β -compound in acetic acid solution at 40 — 50° to acetyl- γ -benziloxime, thus confirming the configurations already assigned (*loc. cit.*). The α -compound is not attacked.

Phenylcarbimide combines with both oximes in ethereal solution with development of heat. The α -compound separates from warm ether in white crystals and melts at 124° ; the β -compound crystallises from dilute alcohol in feathery groups of silky needles and melts at 120° .

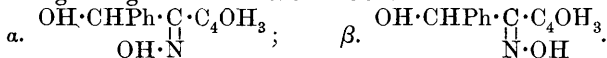
In the preparation of α -furoinoxime (Macnair, *Abstr.*, 1890, 1245), β -furoinoxime is produced at the same time, and separates from ether in slightly yellow groups of crystals melting at 102° . Furoin is much more readily converted into the oximes than benzoin.

The Beckmann rearrangement of the furoinoximes proceeds with difficulty when phosphorus pentachloride is used, more readily with benzenesulphonic chloride. In both cases, a rearrangement of the second type occurs, the α -oxime yielding a nitrile and the β -oxime a carbylamine. Pyromucic acid was obtained on hydrolysing the nitrile with dilute sulphuric acid.

Acetyl- α -furoinoxime, $\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}$, separates from benzene in granular crystals and melts at 113° ; *acetyl- β -furoinoxime* forms groups of needles and melts at 108° . The acetyl group is removed on warming with alcohol.

Phenylcarbimide combines with the furoinoximes, the α -compound, $\text{C}_{17}\text{H}_{14}\text{O}_5\text{N}_2$, forming colourless, star-shaped crystals melting at 56° and becoming dark in air; the β -compound forms needles melting at 120° .

Benzofuroin, $\text{CPh}\cdot\text{CH}(\text{OH})\cdot\text{C}_4\text{OH}_3$, reacts with hydroxylamine in alkaline solution to form a mixture of α -benzofuroinoxime, crystallising from alcohol in small prisms melting at 160° , and β -benzofuroinoxime, which crystallises with difficulty, but forms transparent crystals containing ether, which break up at 35° and then melt at 90° . With benzenesulphonic chloride, the α -oxime yields benzaldehyde and furfuronitrile; the β -oxime yields α -carbylamine. This determines the following configuration for the oximes:



Acetyl- α -benzofuroinoxime, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$, crystallises from benzene and

melts at 115° ; *acetyl-β-furoinoxime* forms needles and melts at 96° .

The compound of phenylcarbimide with α -benzofuroinoxime, $C_{19}H_{16}O_4N_2$, forms an uncrystallisable syrup; the β -compound crystallises from dilute alcohol and melts at 138° .

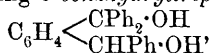
In each pair of oximes here studied, the α -isomeride, in which the hydroxyl and $CHR\cdot OH$ groups occupy the *cis*-position, has a higher melting point and is less soluble than the β -oxime.

C. H. D.

Derivatives of Dihydroisobenzofuran. ALFRED GUYOT and J. CATEL (*Compt. rend.*, 1905, **140**, 254—256. Compare Haller and Guyot, *Abstr.*, 1904, i, 660).—Methylphthalate or methyl *o*-benzoylbenzoate react with magnesium phenyl bromide to give *2-hydroxy-1:1:2-triphenyl-1:2-dihydroisobenzofuran*, $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{CPh}\cdot OH \end{smallmatrix} O$, melting at 118° , and the same compound is obtained by the condensation of magnesium phenyl bromide with diphenylphthalide according to the equation $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ CO \end{smallmatrix} O + MgPhBr = C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{CPh}(OMgBr) \end{smallmatrix} O \rightarrow$

$$C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{CPh}(OH) \end{smallmatrix} O.$$

The authors find that diphenylphthalide is formed as an intermediate compound in the first reactions, methyl phthalate yielding first benzoylbenzoic acid, and then diphenylphthalide, by the action of a small quantity of magnesium phenyl bromide, whilst methyl benzoylbenzoate yields diphenylphthalide and *o*-dibenzoylbenzene under similar conditions. *2-Hydroxy-1:1:2-triphenyl-1:2-dihydroisobenzofuran* condenses readily with phenols or aromatic amines to give derivatives of the type $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \text{CPh}(C_6H_4R) \end{smallmatrix} O$, where $R = \cdot NMe_2$, $\cdot NH_2$, $\cdot OH$, &c., the compounds with dimethylaniline, phenol, and aniline melting at 177° , 167° , and 200° respectively, and is reduced by sodium amalgam in alcoholic solution, yielding *o-benzohydryltriphenylcarbinol*,



melting at 150° .

M. A. W.

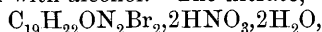
9-Phenylxanthen. RICHARD MEYER (*Ber.*, 1905, **38**, 450—453. Compare Meyer and Saul, *Abstr.*, 1893, i, 471; Ullmann and Engi, *Abstr.*, 1904, i, 682).—9-Phenylxanthen, prepared by distilling fluoran with zinc dust, melts at 138 — 139° , and that prepared by reducing phenylxanthidrol at 144 — 145° . The two products resemble one another in all respects except the melting point.

C. H. D.

Dibromo-additive Compounds of the Cinchona Alkaloids. A. CHRISTENSEN (*J. pr. Chem.*, 1905, [ii], **71**, 1—29. Compare *Abstr.*, 1904, i, 184; Comstock and Koenigs, *Abstr.*, 1892, 1010).—Two isomeric cinchonidine dibromides are formed by adding bromine to the alkaloid in hydrogen bromide and glacial acetic acid solution; α -cin-

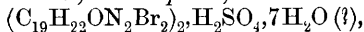
chonidine dibromide crystallises out as the hydrobromide; the β -isomeride is precipitated from the mother liquor as the insoluble nitrate.

α -Cinchonidine dibromide crystallises in large, thin, rhombic, often hexagonal leaflets, blackens at about 200° , melts at about 225° , is optically inactive, and evolves only traces of hydrogen bromide when boiled with alcohol. The nitrate,



crystallises in rosettes or sheaves of long, prismatic needles (Abstr., 1901, i, 481); the hydrobromide, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot 2\text{H}_2\text{O}$, forms a yellow powder consisting of microscopic prisms; the perbromide, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{Br}_2$, crystallises in yellow, quadratic leaflets; the sulphate, $(\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2)_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, crystallises in long needles or prisms, is almost insoluble in cold water, but dissolves easily in dilute sulphuric acid, with formation of an acid sulphate. When treated with concentrated sulphuric acid, α -cinchonidine dibromide forms a sulphonic acid, which crystallises in long, thin needles, evolves hydrogen bromide when boiled with alcoholic potassium hydroxide, and forms an insoluble nitrate, $\text{C}_{19}\text{H}_{21}\text{ON}_2\text{Br}_2 \cdot \text{SO}_3\text{H} \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$.

β -Cinchonidine dibromide crystallises in long prisms, blackens at about 200° , melts at about 210° , has $[\alpha]_D - 135^\circ$ in 2.15 per cent. solution in a mixture of chloroform and alcohol, and, when boiled in 90 per cent. alcohol, is partly converted into bromocinchonidine. The nitrate, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$, crystallises in microscopic, rhombic plates or from boiling water in short prisms (compare Abstr., 1904, i, 520); the hydrobromide, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot 3\text{H}_2\text{O}$, crystallises in long, white, sharp needles; the perbromide, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{Br}_4 \cdot \text{H}_2\text{O}$ (?), crystallises in prisms and is reduced with aqueous sulphurous acid to β -cinchonidine d.bromide; the sulphate,



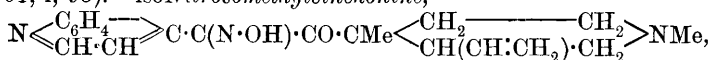
crystallises in needles and at $100-105^\circ$ is partly converted into the sulphonic acid; the insoluble acid sulphate, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{H}_2\text{SO}_4$, formed when an excess of sulphuric acid is added to the solution of the β -dibromide in dilute sulphuric acid, crystallises in thin, colourless hexagonal, rhombic leaflets. The sulphonic acid, formed by the action of concentrated sulphuric acid, does not form an insoluble nitrate or hydrobromide.

Both cinchonidine dibromides yield the same dibromocinchonidine and bromocinchonidine (Abstr., 1904, i, 520). Comstock and Koenigs' α - and β -cinchonine dibromides (Abstr., 1887, 281) are formed by the action of bromine on the alkaloid in hydrogen bromide and glacial acetic acid solution; the hydrobromide of the α -isomeride crystallises from the reaction solution, whilst the β -isomeride is precipitated on addition of ammonia to the mother liquors. α -Cinchonine dibromide crystallises in tufts of small leaflets and has $[\alpha]_D + 179.4^\circ$ in 2.05 per cent. solution in a mixture of chloroform and alcohol. The nitrate, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$, crystallises in feathery aggregates of needles and is only slightly soluble in cold water; the hydrobromide, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr}$, crystallises in long, prismatic needles or pointed prisms; the perbromide, $\text{C}_{19}\text{H}_{22}\text{ON}_2\text{Br}_2 \cdot 2\text{HBr} \cdot \text{Br}_2$, formed by the action of an excess of bromine on the α -dibromide in hydrogen bromide and glacial acetic acid solution, crystallises in microscopic

yellow needles; the sulphate is only slightly soluble in water, but easily soluble in an excess of dilute sulphuric acid.

β -Cinchonine dibromide forms a granular, partly crystalline powder, has $[\alpha]_D +107.5^\circ$ in 1 per cent. solution in a mixture of chloroform and alcohol, and, when boiled with alcohol, is partly converted into bromocinchonine. The *nitrate*, $C_{19}H_{22}ON_2Br_2 \cdot 2HNO_3 \cdot H_2O$, crystallises in long, thin plates; the *hydrobromide*, $C_{19}H_{22}ON_2Br_2 \cdot 2HBr$, forms small crystals resembling octahedra; the sulphate resembles the α -salt. Both cinchonine dibromides, when treated with alcoholic potassium hydroxide, yield the same bromocinchonine. G. Y.

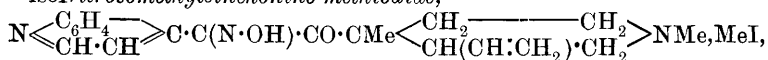
Action of Methyl Iodide on the *iso*Nitroso-compounds of Cinchotoxine and Quinotoxine. GEORG ROHDE and G. SCHWAB (*Ber.*, 1905, 38, 306—320. Compare von Miller and Rohde, *Abstr.*, 1901, i, 95).—*iso*Nitrosomethylcinchonine,



obtained by the action of amyl nitrite and sodium ethoxide on methylcinchonine dissolved in absolute alcohol, crystallises from ethyl acetate in colourless prisms, melts at 158 — 159° , and is best purified through the *hydrochloride*, $C_{20}H_{24}O_2N_3Cl$, which separates from alcohol on adding chloroform in crystals containing the latter, and melts and decomposes at about 230° .

*iso*Nitrosomethylcinchonine *hydriodide*, $C_{20}H_{24}O_2N_3I$, resembles the hydrochloride in separating with chloroform of crystallisation, and melts and decomposes at about 180° .

*iso*Nitrosomethylcinchonine *methiodide*,



separates from methyl alcohol in slightly red crystals and melts and decomposes between 228° and 235° . *iso*Nitrosocinchotoxine *hydriodide*, $C_{19}H_{22}O_2N_3I$, prepared from *isonitrosocinchotoxine*, melts at 85° , subsequently solidifies, and then melts and decomposes at 210° .

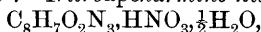
The methiodide, $C_{19}H_{21}O_2N_3, \text{MeI}$, described by von Miller and Rohde (*loc. cit.*), is really identical with the *isonitrosomethylcinchonine* methiodide just described; this would explain the abnormal properties it was supposed to possess. The action of methyl iodide on *isonitrosocinchotoxine* thus gives rise to the methiodide and hydriodide of *isonitrosomethylcinchonine* and to *isonitrosocinchotoxine* hydriodide.

*iso*Nitrosoquinotoxine *hydriodide*, $C_{20}H_{24}O_3N_3I$, prepared by adding the requisite quantity of sodium acetate to a solution of the dihydriodide, melts at 102 — 105° , and, after solidification, at 217° . *iso*-Nitrosomethylquinine, prepared by the action of amyl nitrite on methylquinine, is identical with *isonitrosomethylquinotoxine* (*loc. cit.*); it separates from benzene in wedge-shaped crystals containing benzene and melting at 69 — 71° , but when free from benzene it melts at 156° . The *hydriodide*, $C_{21}H_{26}O_3N_3I$, of *isonitrosomethylquinotoxine* crystallises from alcohol and melts at 207° ; the *methiodide*, $C_{22}H_{28}O_3N_3I$, crystallises from alcohol in slender needles or in nodules, and melts and decomposes at about 163° . The action of methyl iodide on *isonitroso*-

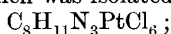
quinotoxine dissolved in chloroform gives *isonitrosomethylquinotoxine* methiodide and *isonitrosomethylquinotoxine* hydriodide.

W. A. D.

Harmine and Harmaline. OTTO FISCHER and CHRISTIAN BUCK (*Ber.*, 1905, **38**, 329—335. Compare *Abstr.*, 1901, i, 405).—When harminic acid is heated with concentrated hydrochloric acid for several hours at 190—200°, it loses only one carboxyl group and gives *apoharminecarboxylic acid*, which crystallises from hot water in slender needles or small plates and is both acid and basic in its properties; the *hydrochloride*, $C_9H_8O_2N_2 \cdot HCl$, *platinichloride*, and *aurichloride* are well defined substances. When heated at 330°, the acid loses carbon dioxide and gives *apoharmine*; towards reducing agents, for example, hydriodic acid or sodium in boiling amyl alcohol, the acid is very stable. *Methylapoharminecarboxylic acid*, $C_{10}H_{10}O_2N_2$, prepared either by methylating *apoharminecarboxylic acid* or by heating methylharmine acid with concentrated hydrochloric acid at 190° for 2 hours, gives a *hydrochloride*, $C_{10}H_{10}O_2N_2 \cdot HCl \cdot H_2O$, crystallising in colourless plates, and a *hydriodide*, $C_{10}H_{10}O_2N_2 \cdot HI$, crystallising in needles. *Nitroapoharminecarboxylic acid*, $C_9H_7O_4N_3$, prepared by direct nitration, crystallises from water in nearly colourless prisms and begins to decompose at about 190°. *Nitroapoharmine nitrate*,



crystallises in reddish-yellow, nodular aggregates. On methylation, *nitroapoharmine* gives *nitromethylapoharmine*, $C_9H_9O_2N_3$, which crystallises from dilute methyl alcohol and decomposes at about 225°; the *hydriodide*, $C_9H_9O_2N_3 \cdot HI$, forms yellow leaflets, the *aurichloride* melts at 174°, and the *platinichloride*, with $2H_2O$, decomposes at 240—245°. *Nitroapoharmine* is not changed when boiled with chromic acid in acetic acid solution; on reduction with tin and hydrochloric acid, it gives *aminoapoharmine*, which was isolated as the *platinichloride*,



this crystallises in golden-yellow prisms and decomposes at 270°.

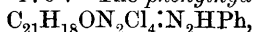
Dihydroapoharmine picrate, $C_8H_{10}O_2 \cdot C_6H_3O_7N_3$, is a crystalline salt which is of service in purifying the base.

When concentrated sulphuric acid is added to harmine dissolved in acetic anhydride, a *harmine-N-sulphonic acid*, $C_{13}H_{12}O_4N_2S$, is obtained, which crystallises in slender needles and is decomposed by boiling dilute hydrochloric acid, giving sulphur dioxide and harmine hydrochloride.

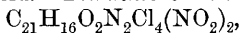
W. A. D.

Chloro-derivatives of Strychnine. GAETANO MINUNNI and F. FERRULLI (*Gazzetta*, 1904, **34**, ii, 364—373).—The following derivatives of the tetrachlorostrychnine obtained by Minunni and Ortoleva (*Abstr.*, 1900, i, 309) have been prepared.

The *hydrochloride*, $C_{21}H_{18}O_2N_2Cl_4 \cdot 2H_2O$, separates from acetic acid solution in white, acicular crystals, which are only slightly soluble in the ordinary solvents and begin to lose hydrogen chloride at 100°, although at 260° they are still unmelted. The free base (+ H_2O) melts and decomposes at 165—170°. The *phenylhydrazone*,

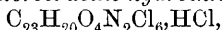


separates from alcohol in minute, yellow crystals, which do not melt at 260° and are soluble in alcohol, benzene, or ethyl acetate and to a slight extent in ether. The *acetyl* derivative, $C_{21}H_{17}O_2N_2Cl_4Ac$, which is very readily soluble in ethyl acetate, and to a less extent in alcohol or benzene, begins to turn brown at about 140° and melts without decomposing at 180 – 197° . The *benzoyl* derivative, $C_{21}H_{17}O_2N_2Cl_4Bz$, separates from ether in crystals which turn brown at about 150° , blacken at 220° , and do not melt at 260° ; it dissolves slightly in alcohol, and readily in ethyl acetate, benzene, or acetic acid. Another *benzoyl* derivative (with H_2O) was also prepared which separates from alcohol in pale yellow crystals softening at 130° and melting and decomposing at 150 – 155° ; it is soluble in ether, alcohol, acetic acid, and ethyl acetate. The action of excess of acetyl chloride on tetrachlorostrychnine in pyridine solution yields *diacetyltrichlorostrychnine*, $C_{21}H_{15}O_2N_2Cl_3Ac_2$, which separates from ether or alcohol in white, acicular crystals melting and decomposing at 185° and dissolving in ethyl acetate or acetic acid. *Tetrachlorodinitrostrychnine*,



is deposited from alcohol in microscopic crystals, which turn brown at about 170° , do not melt at 260° , and dissolve readily in acetic acid or ethyl acetate and to a slight extent in ether or benzene. T. H. P.

Action of Chlorine on Brucine in Glacial Acetic Acid Solution. GAETANO MINUNNI and R. CIUSA (*Gazzetta*, 1904, 34, ii, 361–363).—By passing chlorine into a solution of brucine hydrate in glacial acetic acid, *hexachlorobrucine hydrochloride*,



is obtained as a white, crystalline powder, turning red in the light, and dissolving in alcohol, ethyl acetate, ammonia, or potassium hydroxide solution, or in concentrated sulphuric acid with evolution of hydrogen chloride. The *base* is a white powder, which is turned yellow by light and is soluble in ether, benzene, alcohol, ethyl acetate, or chloroform. Both the base and its hydrochloride turn brown at about 120° , blacken at about 200° , and are still unmelted at 260° . They are not attacked by concentrated nitric acid.

By G. CORONEDI. The hydrochlorides of tetrachlorostrychnine and hexachlorobrucine are non-poisonous and quite innocuous to dogs.

T. H. P.

8-Aminoparaxanthine and its Derivatives. C. F. BOEHRINGER & SÖHNE (D.R.-P. 156901. Compare following abstract).—8-Chloroparaxanthine reacts with ammonia at 150 – 155° in alcoholic solution to form 8-aminoparaxanthine, $C_7H_7O_2N_4 \cdot NH_2$, which blackens at 350° without melting. The *sodium* salt forms colourless needles. 8-Methylaminoparaxanthine sinters at 350° and melts and decomposes at 370° . 8-Dimethylaminoparaxanthine forms long needles and melts at 225° ; the crystalline *sodium* salt dissolves readily in water. 8-Anilino-paraxanthine melts and decomposes at about 340° . C. H. D.

8-Aminotheophylline and its Alkyl and Aryl Derivatives. C. F. BOEHRINGER & SÖHNE (D.R.-P. 156900).—8-Chlorotheophylline

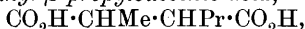
reacts with ammonia or amines on heating in alcoholic solution at 150° , although less readily than 8-chlorocaffeine.

8-Aminotheophylline, $\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{NH} \\ | \quad | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} - \text{N} \end{array} \gg \text{C} \cdot \text{NH}_2$, forms needles and becomes brown at 310° , slowly melting and decomposing. 8-Anilinotheophylline crystallises from alcohol in colourless needles and melts at 320° . 8-Dimethylaminotheophylline forms long needles and melts at about 330° to a colourless liquid. All these derivatives form salts with both acids and bases. C. H. D.

Attempt to Synthesise Hæmopyrrole. L. A. TSCHUGAEFF and N. A. SCHLOESINGER (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1258—1268).—A close connection exists between hæmogoblin and chlorophyll, since both contain a pyrrole nucleus and both are capable of yielding hæmopyrrole under certain conditions. From the work of Küster (Abstr., 1900, i, 68; 1901, i, 58 and 298; 1902, i, 845), it seems probable that hæmopyrrole is 3-methyl-4-propylpyrrole. In an attempt to synthesise the latter compound, the author has prepared the following pyrrole derivatives.

2-Methyl-5-isopropylpyrrole (see Tiemann and Semmler, Abstr., 1897, i, 247) resembles hæmopyrrole in yielding a mercury compound, $(\text{C}_5\text{H}_{12}\text{N})_2\text{Hg} \cdot 4\text{HgCl}_2$, but differs from it in its other reactions.

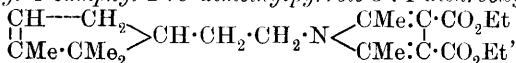
The interaction of ethyl sodiopropylmalonate and ethyl α -bromopropionate yields the ester, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{CPr}(\text{CO}_2\text{Et})_2$, which boils at 276 — 282° and is a viscous liquid with the characteristic odour of polycarboxylic esters. Hydrolysis of this ester by means of sodium hydroxide yields α -methyl- β -propylsuccinic acid,



which crystallises from water in long needles melting at 156 — 157° and is readily soluble in alcohol, ether, and most other organic solvents; when gently heated, it sublimes. The silver salt of this acid, $\text{C}_6\text{H}_{12}(\text{CO}_2\text{Ag})_2$, forms a heavy, curdy precipitate and the ammonium salt a micro-crystalline precipitate soluble in water; the sodium, potassium, uranium, lead, copper, and iron salts were prepared. On heating the ammonium salt for some time at its melting point and subsequently distilling under diminished pressure, it yields the corresponding imide, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CMe} \\ | \\ \text{CO} \cdot \text{CPr} \end{array}$, which boils at 167 — 168° under

20 mm. pressure and sets to a crystalline mass melting at 51 — 53° . The transformation of this imide into 3-methyl-4-propylpyrrole is attended with difficulty, the reaction being possibly brought about to some slight extent by heating the imide with phosphorus trisulphide or pentasulphide. T. H. P.

Ethyl 1-Camphyl-2:5-dimethylpyrrole-3:4-dicarboxylate and its Derivatives. CARL BÜLOW (*Ber.*, 1905, **38**, 189—193. Compare Knorr and Bülow, Abstr., 1884, 1381).—Ethyl diacetylsuccinate readily condenses with an acetic acid solution of camphylamine yielding ethyl 1-camphyl-2:5-dimethylpyrrole-3:4-dicarboxylate,



which crystallises in large, glistening plates melting at 78°. It dissolves in most organic solvents, is odourless and tasteless, and on hydrolysis with aqueous alcoholic potash yields the *potassium* salt, from which the *acid* may be obtained by addition of acetic acid. The acid melts and decomposes at 204°, and on titration with standard potassium hydroxide in presence of phenolphthalein behaves as a monobasic acid. It dissolves readily in alcohol or acetic acid, but is reprecipitated on the addition of water, and is only sparingly soluble in benzene. The *ammonium* salt crystallises in colourless, slender needles, is readily soluble in hot water, and its solution yields precipitates with solutions of calcic, ferric, or cupric chlorides and with silver nitrate.

When heated at 204—210°, the acid is decomposed yielding 1-*camphyl-2:5-dimethylpyrrole* in the form of a viscid, yellow oil, which dissolves readily in most solvents. Its alcoholic solution, when warmed with ferric chloride solution, is turned an intense orange-yellow colour, and a pine shaving dipped in the solution gives a violet-red coloration with concentrated hydrochloric acid.

J. J. S.

4-Methylpyridine. FELIX B. AHRENS (*Ber.*, 1905, **38**, 155—159).—The high boiling fraction of commercial “ β -picoline” was added to the calculated amount of 30 per cent. alcoholic hydrochloric acid, when 2:6-dimethylpyridine hydrochloride separated, whilst from the filtrate the double salt of mercuric chloride and 4-methylpyridine was prepared. 3-Methylpyridine is as chemically active as the corresponding 1-compound.

4:4'-*Dimethyldipyridyl*, prepared by the action of sodium on 4-methylpyridine, was identified by conversion into its various salts. The *aurichloride* does not melt sharply; the *platinichloride* begins to decompose at 250°; the *mercurichloride* melts at 185°, whilst the *picrate* melts and decomposes at 194°.

4-*Allylpyridine mercurichloride*, prepared from the product obtained by interaction of 4-methylpyridine and paraldehyde, crystallises in needles and melts at 150°. The *hydrochloride* forms transparent crystals and melts and decomposes at 247°. The *base* is a colourless liquid and boils at 200—202°; its *platinichloride* melts and decomposes at 206°; its *aurichloride* melts and decomposes at 174°, whilst its *picrate* melts and decomposes at 169—170°.

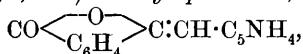
4-Allylpyridine was reduced by sodium ethoxide, the reduction product converted into its nitroso-derivative, from which 4-coniine hydrochloride was prepared. 4-*Coniine* is a colourless liquid and boils at 178—180°. Its *platinichloride* and *hydrochloride* were analysed.

A. McK.

4-Stilbazole. CONRAD FRIEDLÄNDER (*Ber.*, 1905, **38**, 159—160. Compare preceding abstract).—4-*Stilbazole*, prepared by the condensation of 4-methylpyridine and benzaldehyde, separates from alcohol in glistening leaflets and melts at 127°. Its *hydrochloride* forms yellowish-green needles and melts at 204°; the *hydrobromide* forms brownish-red needles and melts at 174°; the *picrate* melts at 213°; the *hydrogen tartrate* melts at 164—165°; the *zincchloride* forms

yellow needles, which soften at about 230° and melt at 250° ; the *aurichloride* forms red needles and melts at 205° ; the *platinichloride* melts at 310° ; the *bromine additive compound*, $C_{13}H_{11}NBr_2$, melts indefinitely at $228-230^{\circ}$.
A. McK.

4-Pyrophthalone. ERICH DÜRING (*Ber.*, 1905, **38**, 161—164. Compare preceding abstracts; Eibner, *Abstr.*, 1901, i, 348, 611; Huber, *Abstr.*, 1903, i, 576).—4-Pyrophthalone,



prepared by the condensation of 4-methylpyridine and phthalic anhydride by zinc chloride, separates from a mixture of ethyl alcohol and glacial acetic acid in glistening, orange-coloured needles, which begin to decompose at 250° . The *hydrochloride* forms red needles; the *mercuric chloride double salt* forms orange-red needles which decompose at about 271° ; the *platinichloride* begins to decompose at 260° . The *sodium salt* is crimson.

Stilbazyl alcohol, $OH \cdot CH_2 \cdot C_6H_4 \cdot CH:CH \cdot C_5NH_4$, prepared by the reduction of 4-pyrophthalone in glacial acetic acid solution by zinc dust, forms the *hydrochloride*, which is bright yellow and begins to decompose at 210° ; the *hydrobromide* decomposes at 230° ; the *nitrate* melts at $160-165^{\circ}$; the *aurichloride* decomposes at $165-167^{\circ}$; the *platinichloride* melts and decomposes at 185° .

Tetrachloro-4-pyrophthalone, $CO \begin{array}{c} \diagup \text{O} \diagdown \\ \text{C}_6\text{Cl}_4 \end{array} C:CH \cdot C_5NH_4$, prepared from 4-methylpyridine and tetrachlorophthalic anhydride, forms a dark green powder.
A. McK.

Reduction Products of 4'-Methyl-4-stilbazole. 4- ω -Trichloro-hydroxypropylpyridine. ERICH DÜRING (*Ber.*, 1905, **38**, 164—167. Compare preceding abstracts).—4'-Methyl-4-stilbazole, $C_6H_4Me \cdot CH:CH \cdot C_5NH_4$, prepared by the condensation of 4-methylpyridine with *p*-tolualdehyde, separates from alcohol in white crystals, which soften at 80° and melt at $101-102^{\circ}$. Its *hydrochloride* melts at 120° ; its *hydrobromide* melts at $176-177^{\circ}$; its *mercurichloride* softens at 195° and begins to melt at 208° ; its *aurichloride* melts and decomposes at 191° ; its *platinichloride* melts and decomposes at 193° .

When reduced by hydriodic acid and red phosphorus, 4'-methyl-4-stilbazole forms 4'-methyl-4-stilbazole, $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot C_5NH_4$, a colourless liquid which boils at 220° under 80 mm. pressure; the *hydrochloride* softens at 135° and begins to melt at 140° ; the *hydrobromide* melts at $149-150^{\circ}$; the *hydriodide* softens at 132° and melts at 138° ; the *mercurichloride* melts indefinitely at 110° ; the *aurichloride* melts at 155° ; the *platinichloride* melts and decomposes at 194° .

4'-Methyl-4-stilbazoline, $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot C_5NH_{10}$, prepared by the reduction of 4'-methyl-4-stilbazole by sodium ethoxide, is a colourless liquid which boils at 215° ; its *platinichloride* melts and decomposes at 205° .

4- ω -Trichloro- β -hydroxypropylpyridine, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot C_5NH_4$,

prepared from 4-methylpyridine and chloral, forms glistening plates and melts at 160° ; its *platinichloride* melts and decomposes at 198° .

A. McK.

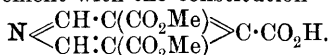
Pyridine-2:3:4-tricarboxylic Acid. ALFRED KIRPAL (*Monatsh.*, 1905, **26**, 53—64).—The *anhydride* of pyridine-2:3:4-tricarboxylic acid is formed when the tricarboxylic acid is warmed with acetic anhydride at 30 — 40° ; it melts at 170° , and when heated on the water-bath with acetic anhydride yields cinchomeronic anhydride, which is also formed when the tricarboxylic acid is boiled with acetic anhydride. The tricarboxylic anhydride is therefore to be represented

by the formula
$$\begin{array}{c} \text{CH:CH} \text{---} \text{C} \cdot \text{CO} \\ \text{N}=\text{C}(\text{CO}_2\text{H}) \cdot \text{C} \cdot \text{CO} \end{array} \text{>O},$$
 and Meyer's anhydride chloride

(Abstr., 1901, i, 750) by
$$\begin{array}{c} \text{CH:CH} \text{---} \text{C} \cdot \text{CO} \\ \text{N}=\text{C}(\text{COCl}) \cdot \text{C} \cdot \text{CO} \end{array} \text{>O}.$$
 The 3-methyl ester,

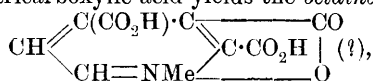
$$\begin{array}{c} \text{CH:CH} \text{---} \text{C} \cdot \text{CO}_2\text{H} \\ \text{N}=\text{C}(\text{CO}_2\text{H}) \cdot \text{C} \cdot \text{CO}_2\text{Me} \end{array}$$
 (compare Wegscheider, Abstr., 1902, i, 618), is

formed by warming the anhydride with methyl alcohol; it crystallises in glistening plates, melts at 170° , and when heated with methyl-alcoholic hydrogen chloride yields the trimethyl ester, which melts at 102° (m. p. 97° , Meyer, *loc. cit.*). The action of aqueous ammonia on the 3-methyl ester leads to the formation of the *ammonium* salt of the monamic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_5\text{NH}_2(\text{CO}_2\text{NH}_4)_2$, which crystallises in colourless, flat needles, loses $1\text{H}_2\text{O}$ at 100° , and melts and decomposes at 150° . The *amic* acid, $\text{C}_8\text{H}_6\text{O}_5\text{N}_2$, crystallises in colourless prisms, melts at 180° , and when heated above its melting point yields cinchomeronimine. The dimethyl ester melts at 183° (Rint, Abstr., 1897, i, 485, gives m. p. 166°) and yields traces of the trimethyl ester on prolonged boiling with methyl-alcoholic hydrochloric acid, in agreement with the constitution



Contrary to expectation, the diethyl ester of pyridine-2:3:4-tricarboxylic acid yields diethyl cinchomeronate when heated at 150 — 160° or with alcoholic hydrochloric acid under pressure, which points to

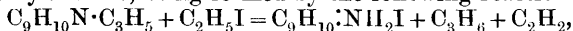
the constitution
$$\text{N} \begin{array}{c} \text{CH} \cdot \text{C}(\text{CO}_2\text{Et}) \\ \text{CH} \cdot \text{C}(\text{CO}_2\text{H}) \end{array} \text{>C} \cdot \text{CO}_2\text{Et}.$$
 When warmed in a reflux apparatus with methyl iodide and aqueous sodium carbonate, pyridine-2:3:4-tricarboxylic acid yields the *betaine*,



which crystallises in small, colourless prisms, becomes brown at 180° , melts and decomposes at 220° , and when boiled with water yields apophyllenic acid.

G. Y.

Action of Allyl Iodide on Tetrahydroquinoline. EDGAR WEDEKIND (*Ber.*, 1905, **38**, 436—440).—The compound described by Wedekind and Oechslen (Abstr., 1903, i, 116) as 1-allyltetrahydroquinoline hydriodide does not contain allyl, and is really tetrahydroquinoline hydriodide, being formed by the following reaction:



the allyl group being expelled from the tertiary base by the action of ethyl iodide. The reaction between allyl iodide and tetrahydroquinoline proceeds differently in the presence or absence of alcohol; in the first case, addition taking place to form 1-allyltetrahydroquinoline hydriodide, and in the second hydrogen iodide being formed, which combines with unaltered tetrahydroquinoline to form the hydriodide, allyltetrahydroquinoline remaining as the free base.

A repetition of the reaction between ethylene iodide and ethyl tetrahydroisoquinolino-2-acetate (Wedekind, Abstr., 1904, i, 96) has shown that the principal product is the hydriodide of the ester, $C_{28}H_{38}O_4N_2I_2$, melting at $153-154^\circ$. It was not found possible to obtain again the iodide melting at $168-169^\circ$. C. H. D.

7-Aminoquinaldine [7-Amino-2-methylquinoline]. E. ALBER (*J. pr. Chem.*, 1905, [ii], 71, 39-54. Compare Doebner and Miller, Abstr., 1884, 1373; Gerdeisen, Abstr., 1889, 520).—The action of nitric acid of sp. gr. 1.49 on benzylacetone at -18° leads to the formation of a mixture of *p*- and *o*-nitrobenzylacetones. *p*-Nitrobenzylacetone, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot COMe$, crystallises in long, white needles, melts at 42° , boils at 204° under 13 mm. pressure, and is identical with Wortsman's product (*Inaug. Diss.*, Basel, 1903), obtained by hydrolysis of ethyl *p*-nitrobenzylacetonedicarboxylate. The phenylhydrazone of *p*-nitrobenzylacetone forms yellow crystals, melts at 103° , and decomposes on exposure to light, more slowly in the dark.

op-Dinitrobenzylacetone is formed by the action of nitric acid of sp. gr. 1.52 on the mononitro-compounds in concentrated sulphuric acid, or on benzylacetone in fuming sulphuric acid at -18° . It crystallises in small, colourless, rhombic leaflets, in long prisms, or in large plates, melts at $58-59^\circ$, and, when warmed with aqueous potassium hydroxide, forms a dark red solution.

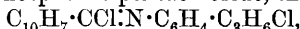
A reduction of the dinitro-compound with stannous chloride and concentrated hydrochloric acid leads to the formation of 7-amino-2-methylquinoline, which crystallises in long, slender, colourless needles, melts at 148° , is easily volatile in a current of steam, forms a violet-blue fluorescent solution in ether, which shows a green fluorescence when poured into water, and when diazotised and "coupled" with β -naphthol in alkaline solution forms a dark red dye. The hydrochloride crystallises in microscopic, yellow needles and dissolves in water to a solution with intensely green fluorescence; the tin double salt crystallises in leaflets and dyes tannated cotton-wool yellow; these salts give the pine-wood pyrrole reaction. The benzoyl derivative, $C_{17}H_{14}ON_2 \cdot H_2O$, crystallises in small, white needles, loses H_2O at 100° , melts at $172-173^\circ$, and forms a fluorescent blue solution in dilute hydrochloric acid. The acetyl derivative, $C_{12}H_{12}ON_2$, crystallises in long, yellow needles, melts at 192° , is easily soluble in alcohol, but only slightly so in benzene or petroleum, dissolves in dilute acids to blue fluorescent solutions, and gives the pine-wood reaction. The picrate, $C_{10}H_{10}N_2 \cdot C_6H_3O_7N_3$, crystallises in long, yellow needles and melts at $213-214^\circ$.

The properties described show the author's 7-amino-2-methyl-

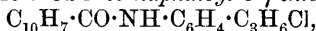
quinoline to be isomeric, and not identical, with Doebner and Miller's base (*loc. cit.*), obtained by reduction of 7-nitro-2-methylquinoline.

G. Y.

α -Naphthoyltetrahydroquinoline. JULIUS VON BRAUN (*Ber.*, 1905, **38**, 179—181).— α -Naphthoyl chloride, prepared by the action of phosphorus pentachloride on α -naphthoic acid, is a transparent liquid and boils at 172—173° under 15 mm. pressure. 1- α -Naphthoyltetrahydroquinoline, $C_6H_4 \begin{smallmatrix} \text{N}(\text{CO} \cdot C_{10}H_7) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} CH_2$, prepared by shaking α -naphthoyl chloride with an alkali hydroxide and tetrahydroquinoline, forms colourless crystals and melts at 115°. When the amide is gradually heated at 160° with phosphorus pentachloride, the acid chloride,



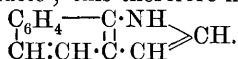
first formed, is transformed into *naphthoyl-o- γ -chloropropylanilide*,



which forms red crystals and melts at 133°.

A. McK.

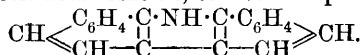
Constitution of α -Naphthindole. ROBERT PSCHORR and E. KUHTZ (*Ber.*, 1905, **38**, 217—219).— α -Naphthindole is easily prepared, in a manner analogous to Hinsberg's preparation of β -naphthindole (*Abstr.*, 1888, 372), by distillation of α -naphthoxindole with zinc dust, and is identical with Schlieper's naphthindole (*Abstr.*, 1887, 153, 963). To settle whether the nitrogen ring is attached to the naphthalene ring at the 1:2 or 1:8 position, an attempt was made to condense 1-amino-2-ethoxynaphthalene and 1-aminonaphthalene-8-sulphonic acid (in which the 2 and 8 positions respectively are already occupied) with glyoxal sodium bisulphite by Hinsberg's method. Only in the latter compound, substituted in the 8 position, was a naphthindole derivative, *α -naphthindoledisulphonic acid*, obtained, which, on heating with zinc dust, was converted into naphthindole; this therefore has the constitution



E. F. A.

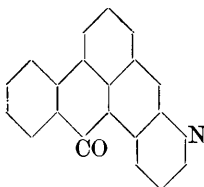
2:2-Dinaphtha-1:1-imine [$\alpha\alpha$ -Di- β -naphthacarbazole]. VICTOR VESELY (*Ber.*, 1905, **38**, 136—139. Compare Nietzki and Goll, *Abstr.*, 1886, 245; Meissenheimer and Witte, *Abstr.*, 1904, i, 193).—2-Chloro-1-nitronaphthalene, $C_{10}H_6O_2NCl$, prepared from 1-nitro- β -naphthylamine by Votócek and Zeníšek's method (*Abstr.*, 1900, i, 19), crystallises in yellow needles, melts at 95·5°, distils without decomposition above 360°, and is reduced by zinc dust in glacial acetic acid solution to 2-chloro- α -naphthylamine (Cleve, *Abstr.*, 1887, 961). 2-Bromo-1-nitronaphthalene, obtained in the same manner, crystallises in slender, yellow needles, melts at 102—103°, and distils, without decomposition, above 360°.

When boiled with copper powder in nitrobenzene solution, 2-iodo-1-nitronaphthalene (Meldola, *Trans.*, 1885, **47**, 521) yields 1:1-dinitro-2:2-dinaphthyl, $C_{20}H_{12}O_4N_2$, which crystallises in colourless scales, commences to blacken at 265°, melts at 276°, and is reduced by zinc dust, in glacial acetic acid solution, to 2:2-dinaphtha-1:1-imine,



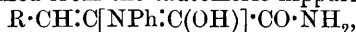
This is identical with Nietzki and Goll's dinaphthacarbazole (*loc. cit.*). The constitution of the two bases obtained by these authors from 1:1-hydrazonaphthalene must be $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{NH}_2) \cdot \text{C} - \text{C} \cdot \text{C}(\text{NH}_2) \\ | \qquad | \\ \text{CH} = \text{CH} \quad \text{CH} = \text{CH} \end{array} \text{C}_6\text{H}_4$ for dinaphthylene, and $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{CH} \cdot \text{CH} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{CH} \cdot \text{CH} \end{array} \text{C} \cdot \text{NH}_2$ for naphthidine. G. Y.

Syntheses in the Anthracene Series and New Dyes. OSCAR BALLY (*Ber.*, 1905, **38**, 194—196).—When β -aminoanthraquinone is condensed with glycerol as in the ordinary Skrap's synthesis, the product is not Graebe's anthraquinolinequinone (*Annalen*, 1880, **201**, 349), but *benzanthronequinoline*, $\text{C}_{20}\text{H}_{11}\text{ON}$, which crystallises from toluene in needles melting at 251° . The same compound is also formed when anthraquinonequinoline is condensed with glycerol, and is represented by the formula

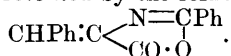


Anthranol or anthraquinone readily condenses with glycerol, yielding *benzanthrone* itself, $\text{C}_{17}\text{H}_{10}\text{O}$, which melts at 170° . Compounds of this type, when fused with alkali, yield dyes. J. J. S.

Azactones [Alkylideneoxazolones] and their Transformations. EMIL ERLNMEYER, jun. (*Annalen*, 1904, **337**, 265—271. Compare Abstr., 1902, i, 595; this vol., i, 131).—Although α -aminoacids and their mono-alkyl derivatives readily yield dimolecular anhydrides, hippuric acid is not capable of such a reaction, but its alkylidene derivatives, $\text{R} \cdot \text{CH} : \text{C}(\text{NHBz}) \cdot \text{CO}_2\text{H}$, on the other hand, give internal anhydrides. Since these anhydrides are converted by ammonia into amides, $\text{R} \cdot \text{CH} : \text{C}(\text{NHBz}) \cdot \text{CO} \cdot \text{NH}_2$, which lose water and yield compounds possessing the characters of acid imides, and having the probable formula $\text{CHPh} : \text{C} \begin{array}{c} \text{N} = \text{CPh} \\ | \\ \text{CO} \cdot \text{NH} \end{array}$, it seems likely that the anhydrides are formed from the tautomeric hippuric acids,



and consequently are represented by the formula



The name "azactone" [alkylideneoxazolone] is given to such anhydrides of the general form $\text{R} \cdot \text{CH} : \text{C} \begin{array}{c} \text{N} = \text{CR} \\ | \\ \text{CO} \cdot \text{O} \end{array}$, a formula which accounts for their formation from α -acylaminoacids only and their yellow colour. The latter depends not only on the ring, but also on the nature and position of the substituting groups. K. J. P. O.

Azlactones [Alkylideneoxazolones] from Cinnamaldehyde or Cuminaldehyde and Hippuric Acid. EMIL ERLÉNMEYER, jun., and O. MATTER (*Annalen*, 1904, **337**, 271—282. Compare preceding abstract).—On heating cinnamaldehyde, hippuric acid, and sodium acetate with acetic anhydride at 100°, the *azlactone* [2-phenyl-4-cinnamylideneoxazolone], $\text{CHPh}:\text{CH}:\text{CH}:\text{C} \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, is obtained as orange-yellow needles melting at 152°, which can only be purified by conversion into cinnamylidenehippuric acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{C}(\text{NHBz})\cdot\text{CO}_2\text{H}$, by warming with aqueous sodium hydroxide; it crystallises in yellow needles, melting and decomposing at 238°, and is reconverted into the azlactone by heating with acetic anhydride. After prolonged heating with hydrochloric acid under pressure at 120°, the acid is decomposed into carbon dioxide, benzoic acid, naphthalene, and α -naphthoic acid. The intermediate unsaturated ketonic acid, $\text{CHPh}:\text{CH}:\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, could not be isolated. The *ethyl* ester of cinnamylidenehippuric acid, prepared by dissolving the acid in alcoholic sodium hydroxide, crystallises in colourless needles melting at 132°.

Cuminaldehyde and hippuric acid yield the *azlactone* [2-phenyl-4-cumylideneoxazolone], $\text{C}_6\text{H}_4\text{Pr}^\beta:\text{CH}:\text{C} \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, which crystallises in yellow needles melting at 121°.

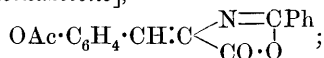
Cumylidenehippuric acid, $\text{C}_6\text{H}_4\text{Pr}^\beta:\text{CH}:\text{C}(\text{NHBz})\cdot\text{CO}_2\text{H}$, is obtained as colourless needles melting at 201° by dissolving the azlactone in sodium hydroxide; the *methyl* ester forms crystals melting at 128°, and the *ethyl* ester colourless needles melting at 164°. The *amide* prepared by treating the azlactone with ammonia crystallises in colourless needles melting at 170°. When warmed with sodium hydroxide, it yields the *imide*, $\text{C}_6\text{H}_4\text{Pr}^\beta:\text{CH}:\text{C} \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, which crystallises in yellow needles melting at 245°. If the azlactone is boiled for 3 to 4 hours with sodium hydroxide (3 mols.), the *sodium* salt of *p-isopropylphenylpyruvic acid*, $\text{C}_6\text{H}_4\text{Pr}^\beta:\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, is obtained; the free *acid* crystallises in leaflets melting at 78°, decomposes in the air, and gives a green coloration with ferric chloride. The keto-acid condenses with benzaldehyde in the presence of concentrated hydrochloric acid, yielding the *oxylactone*, $\text{C}_6\text{H}_4\text{Pr}^\beta:\text{CH} \begin{smallmatrix} \text{CHPh}\cdot\text{O} \\ \text{CO} \text{---} \text{CO} \end{smallmatrix}$, which crystallises in colourless leaflets, melting at 212°, and giving a green coloration with ferric chloride.

K. J. P. O.

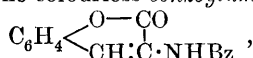
Azlactones [Alkylideneoxazolones] from Furfuraldehyde, or Salicylaldehyde and Hippuric Acid. EMIL ERLÉNMEYER, jun., and WERNER STADLIN (*Annalen*, 1904, **337**, 283—293. Compare preceding abstracts).—Furfuraldehyde and hippuric acid yield the *azlactone* [2-phenyl-4-furfurylideneoxazolone], $\text{C}_4\text{OH}_3:\text{CH}:\text{C} \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$, which crystallises in golden-yellow needles melting at 171°; by warming with dilute sodium hydroxide, it is converted into *furfurylidene-*

hippuric acid, $C_4OH_3 \cdot CH : C(NHBz) \cdot CO_2H$; the latter crystallises in leaflets melting at 210° . The *methyl* ester is formed when the azlactone is warmed with a methyl-alcoholic solution of potassium hydroxide and crystallises in leaflets melting at 141° , and the *ethyl* ester in colourless needles melting at 132 — 133° . The *amide* is prepared by the action of ammonia on the azlactone, and forms pale yellow needles melting at 184° . The *imide*, $C_4OH_3 \cdot CH : C \begin{smallmatrix} \text{N}=\text{CPh} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$, prepared by warming the amide with sodium hydroxide solution, is an intensely yellow, insoluble substance decomposing at 241° . The *piperidide*, $C_4OH_3 \cdot CH : C(NHBz) \cdot CO \cdot C_5NH_{10}$, is obtained by warming the azlactone with alcoholic piperidine solution, as colourless needles melting at 162 — 163° .

The interaction of salicylaldehyde and hippuric acid has been previously studied by Plöchl, Wolfrum, and Rebuffat (*Ber.*, 1885, **18**, 1183), who isolated two substances, one a yellow substance, $C_{32}H_{24}O_7N_2$ or $C_{16}H_{13}O_4N$, which is now shown to be the azlactone [*2-phenyl-4-o-acetoxybenzylideneoxazolone*],

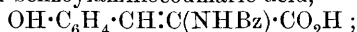


the other substance is the colourless *benzoylaminocoumarin*,



which was thought to be benzoyliminocoumarin. These two substances are formed from the normal primary product, *benzoylaminocoumaric acid*, $OH \cdot C_6H_4 \cdot CH : C(NHBz) \cdot CO_2H$, which then loses water in two different ways, possibly from the two stereoisomeric forms. The substance which is formed from the coumarone by the action of sodium hydroxide is not salicylglycidic acid, but *o-hydroxyphenylpyruvic acid*, which immediately condenses to oxycoumarin, $C_6H_4 \begin{smallmatrix} O-CO \\ \text{CH}_2 \cdot CO \end{smallmatrix}$.

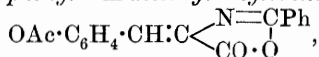
The azlactone is prepared by heating hippuric acid, salicylaldehyde, and sodium acetate with acetic anhydride on the water-bath, and is contained in the first alcoholic extracts of the product, whilst the benzoylaminocoumarin is found in the last extracts; it crystallises in pale yellow leaflets melting at 137 — 138° , and is converted by heating with 10 per cent. sodium hydroxide into benzoylaminocoumarin and benzoylaminocoumaric acid,



the latter forms colourless crystals melting at 185° . Benzoylaminocoumarin crystallises in needles melting at 172 — 173° , and is insoluble in sodium carbonate solution. When either the azlactone or benzoylaminocoumarin is boiled with sodium hydroxide, the oxycoumarin is obtained as needles melting at 152° , which give a green coloration with ferric chloride. It yields a *phenylhydrazone*, $C_{15}H_{12}O_2N_2$, which crystallises in yellow plates melting at 173 — 174° , and also condenses with *o*-phenylenediamine giving the compound $C_{15}H_{10}ON_2$, which crystallises in colourless needles melting at 230° . The azlactone could not be converted into an ester.

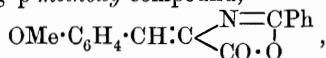
Attempts to obtain isomerides of tyrosine from benzoylamino-coumaric acid were not successful.
K. J. P. O.

Azlactones [Alkylidenexazolones] formed in the Condensation of *m*-Hydroxybenzaldehyde or Anisaldehyde with Hippuric Acid. EMIL ERLÉNMEYER, jun., and FRITZ WITTENBERG (*Annalen*, 1904, 337, 294—301. Compare preceding abstracts).—The acetylazlactone [2-phenyl-4-m-acetoxybenzylidenexazolone],

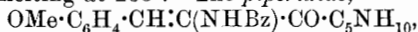


is prepared from *m*-hydroxybenzaldehyde and hippuric acid, and forms crystals melting at 145°; when treated with sodium hydroxide, the *m*-hydroxybenzylidenehippuric acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{NHBz}) \cdot \text{CO}_2\text{H}$, is obtained as crystals melting at 204°; the ethyl ester crystallises in needles melting at 118°; the piperidide, which is prepared by heating the azlactone with alcoholic piperidine, crystallises in colourless needles melting at 201°.

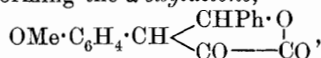
The corresponding *p*-methoxy-compound,



is prepared from anisaldehyde and hippuric acid, and crystallises in yellow needles melting at 156.5°; when warmed with sodium hydroxide, *p*-methoxybenzylidenehippuric acid, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{NHBz}) \cdot \text{CO}_2\text{H}$, is formed as colourless needles melting and decomposing at 225°; the methyl ester, prepared from the azlactone and methyl alcoholic sodium hydroxide, forms colourless leaflets melting at 153°, and the amide, prepared from the azlactone and ammonia, colourless crystals melting at 187°. The imide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{array}{l} \text{N}=\text{CPh} \\ \text{CO} \cdot \text{NH} \end{array}$, prepared from the amide by the action of sodium hydroxide, crystallises in yellow needles melting at 283°. The piperidide,



prepared from the azlactone and alcoholic piperidine, crystallises in colourless leaflets melting at 173°. *p*-Methoxyphenylpyruvic acid, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$, is obtained by boiling the azlactone for several hours with a slight excess of 10 per cent. sodium hydroxide, and crystallises in prisms melting at 186°; it gives a green coloration with ferric chloride and decomposes on keeping. Its phenylhydrazone, $\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_2$, crystallises in colourless leaflets melting at 154°. In the presence of concentrated hydrochloric acid, the keto-acid condenses with benzaldehyde, forming the α -oxylactone,

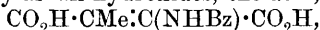


which crystallises in prisms with 1 mol. of alcohol, melting at 180°.

K. J. P. O.

Condensation of Pyruvic Acid with Hippuric Acid. EMIL ERLÉNMEYER, jun., and E. ARBENZ (*Annalen*, 1904, 337, 302—306. Compare preceding abstracts).—The condensation of pyruvic acid with hippuric acid was first investigated by Hoffmann (*Ber.*, 1886, 19,

2555), who obtained a compound which is now shown to be the carboxylic acid, $\text{CO}_2\text{H}\cdot\text{CMe}\cdot\text{C}\begin{smallmatrix} \nearrow \text{N}=\text{CPh} \\ \searrow \text{CO}\cdot\text{O} \end{smallmatrix}$; it forms colourless crystals melting at 157° . By alkali hydroxides, the acid,



is probably formed, but on setting it free from its salts is immediately reconverted into the azlactone. When the azlactone is boiled with barium carbonate, the *barium* salt, $\text{C}_{12}\text{H}_9\text{O}_5\text{NBa}\cdot 2\text{H}_2\text{O}$, is formed.

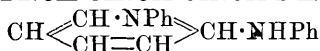
When treated with dilute sulphuric acid, the azlactone undergoes the characteristic decomposition, ammonia, benzoic acid, and methyl-oxalacetic acid being produced; the latter, however, decomposes into carbon dioxide and methylpyruvic acid, which was identified by means of a characteristic barium salt, and its phenylhydrazone, and in addition by its conversion into scatolecarboxylic acid and scatole.

K. J. P. O.

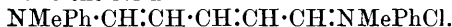
Methylation of Dibenzenesulphonebenzidine. OSCAR HINSBERG (*Ber.*, 1905, 38, 554. Compare Abstr., 1893, i, 168; Willstätter and Kalb, Abstr., 1904, i, 1050).—Dibenzenesulphonedimethylbenzidine, prepared by heating dibenzenesulphonebenzidine with methyl iodide, methyl alcohol, and aqueous sodium hydroxide under pressure at 100° , melts at $189\text{--}190^\circ$. When the reaction takes place in an open vessel, the methylation is not complete; the melting point $179\text{--}180^\circ$, previously observed, was that of a mixture so obtained.

G. Y.

Action of Secondary Aromatic Amines on Dinitrophenylpyridinium Chloride. THEODOR ZINCKE and W. WÜRCKER (*Annalen*, 1905, 338, 107—141).—It has been shown that primary aromatic bases such as aniline interact with dinitropyridinium chloride, yielding, besides dinitroaniline, a red salt of a univalent base, for which either the formula $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHPh}$ or



was suggested. König imagines that the substance is desmotropic, and can be represented by either formula. Similar compounds have now been obtained by the action of methylaniline on the pyridinium chloride, which is decomposed by alkali hydroxides, giving the aldehyde, $\text{NMePh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$, and methylaniline. The original salt must therefore have the formula



The methylaniline group can easily be replaced by an oxime or hydrazone group, or by aniline or *p*-chloroaniline. These reactions are all in favour of the open chain formula.

Dinitrophenylpyridinium chloride is heated in alcoholic solution with methylaniline and the product poured into dilute hydrochloric acid; the compound $\text{NMePh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NMePhCl}$ crystallises with $1\frac{1}{2}\text{H}_2\text{O}$ from water and with HCl and 3MeOH from methyl-alcoholic hydrochloric acid, and melts and decomposes at $116\text{--}118^\circ$; it forms a colourless solution in concentrated sulphuric acid, but yields a red sulphate. Its acetic acid solution gives a brownish-red

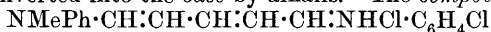
precipitate with potassium dichromate, and its alcoholic solution with potassium tri-iodide a *periodide*, which crystallises in violet needles melting and decomposing at 170—172°.

Methyl-*p*-bromoaniline (which is a yellow oil boiling at 136—138° under 12 mm. pressure) and the pyridinium salt react giving the compound $C_6H_4Br \cdot NMe \cdot CH:CH:CH:CH:CH:NCI \cdot Me \cdot C_6H_4Br$, which crystallises in red leaflets or needles, sintering at 200° and melting and decomposing at 205—208°; it dissolves without colour in concentrated sulphuric acid; on dilution, the *sulphate* is precipitated as red flocks. The *platinichloride*, $(C_{19}H_{19}Br_2N_9)_2PtCl_6$, is a brick-red, crystalline powder sintering at 170°, melting and decomposing at 187°.

When the methylaniline compound is boiled with 20 per cent. methyl-alcoholic sodium carbonate solution and the product acidified with acetic acid, the compound $NMePh \cdot CH:CH:CH:CH \cdot CHO$ is obtained as yellow needles melting and decomposing at 78—80°; it is soluble in dilute acids, but rapidly decomposed by them with the formation of methylaniline; it reduces an ammoniacal silver solution. It yields an *oxime* and a *phenylhydrazone*, which are also formed directly from the original methylaniline compound. It reacts with primary and secondary arylamines, and with methylaniline regenerates the original material. It forms double salts and a crystalline *platinichloride*, $(C_{12}H_{14}ON)_2PtCl_6$, which is a reddish-brown powder melting and decomposing at 157—160°. The *picrate* forms pale brown needles melting and decomposing at 142—144°.

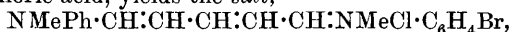
The aldehyde, $C_6H_4Br \cdot NMe \cdot CH:CH:CH:CH \cdot CHO$, obtained in a similar manner to the compound just described, crystallises in yellow plates or flattened needles melting and decomposing at 116—117°; its salts are unstable, and the *platinichloride*, $(C_{12}H_{13}ONBr)_2PtCl_6$, is a pale brown, unstable powder. The *oxime* crystallises in pale yellow needles melting and decomposing at 115—117° and is insoluble in alkali hydroxides, but is dissolved and decomposed by acids; its solution in concentrated sulphuric acid has a blood-red coloration. The *phenylhydrazone* crystallises in pale yellow leaflets readily decomposed by acids.

The compound $NMePh \cdot CH:CH:CH:CH:CH:CH:NHPhCl$ is prepared by treating the aldehyde with aniline and hydrochloric acid, and crystallises in ruby-red needles melting and decomposing at 159—161°; the salt is converted into the *base* by alkalis. The compound



is prepared from the aldehyde and *p*-chloroaniline, and crystallises in red leaflets melting and decomposing at 115—118°; when boiled with hydrochloric acid, it is converted into *chlorophenylpyridinium chloride*. The free *base*, $C_{18}H_{17}N_2Cl$, is very stable and crystallises in needles which are dark brown by reflected and pale yellow by transmitted light; it melts and decomposes at 127°.

The aldehyde, $C_{12}H_{13}ON$, when treated with methyl-*p*-bromoaniline and hydrochloric acid, yields the *salt*,



which forms a dark red, crystalline powder sintering and then melting and decomposing at 144°.

The compound $C_6H_4Br \cdot NMe \cdot CH:CH:CH:CH:CH:NMePhCl$ is

formed from the aldehyde, $C_{12}H_{12}ONBr$, and methylaniline and is a purplish-red, crystalline powder melting and decomposing at $111-112^{\circ}$.

Cinnamaldehyde and methylaniline yield an unstable compound, $CHPh:CH:CH:NMePhCl$, which forms a *mercurichloride*, crystallising in orange-red needles, melting and decomposing at $167-169^{\circ}$, and a *platinichloride* which forms yellow crystals.

The methylaniline compound is decomposed by aniline and *p*-chloroaniline, both methylaniline groups being replaced by aniline groups. The *oxime*, $NHPh:CH:CH:CH:CH:CH:NOH$, and the *phenylthydrazone*, $NHPh:CH:CH:CH:CH:N_2HPh$, of the dianilide which was previously described have now been prepared; the former crystallises in yellow needles melting and decomposing at 146° , and the latter in yellow leaflets melting and decomposing at 135° . K. J. P. O.

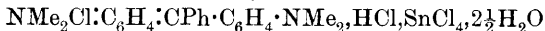
Malachite-green and Crystal-violet. RUDOLF LAMBRECHT and HUGO WEIL (*Ber.*, 1905, **38**, 270—282. Compare *Abstr.*, 1904, i, 877).—*Tetramethyldiaminotriphenylcarbothiol*, $SH \cdot CPh:(C_6H_4 \cdot NMe_2)_2$, obtained by passing hydrogen sulphide into a cold alcoholic solution of malachite-green containing acetic acid, crystallises from a mixture of benzene and alcohol as a colourless powder and melts at 153° ; the analogous compound, $SH \cdot C(C_6H_4 \cdot NMe_2)_3$, obtained from crystal-violet, melts at 159° . The same substances are obtained by using ammonium sulphide or sodium polysulphides instead of hydrogen sulphide. *Tetramethyldiaminothiobenzophenone*, $C_{17}H_{20}N_2S$, is obtained from the mother liquors of the carbothiol of crystal-violet, and crystallises from alcohol in steel-blue needles melting at 202° . The carbothiols are not decomposed when heated with benzene and sodium hydroxide or metallic sodium, but are reduced on boiling with alcohol through which hydrogen sulphide is passed to form leuco-malachite-green and leuco-crystal-violet.

When the carbothiol of malachite-green is heated with dilute acetic acid, it is rapidly decomposed, giving hydrogen sulphide and a solution of the quinonoid salt of the malachite-green base; on the other hand, an excess of dilute mineral acids under similar conditions only slowly eliminates hydrogen sulphide from the carbothiols, although the theoretical quantity of a dilute mineral acid brings about the loss of hydrogen sulphide at 50° .

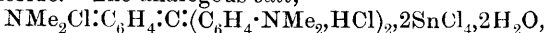
The nature of the following salts illustrates the gradual production of colour from triphenylcarbinol bases.

Colourless Salts.—The *stannichloride* of *tetramethyldiaminotriphenylcarbothiol*, $C_{25}H_{26}N_2S, 2HCl, SnCl_4, \frac{1}{2}H_2O$, is obtained by dissolving the carbothiol in ice-cold hydrochloric acid and adding stannic chloride. The analogous *derivative*, $C_{25}H_{31}N_3S, 3HCl, 1\frac{1}{2}SnCl_4, 1\frac{1}{2}H_2O$, of crystal-violet is also colourless.

Orange-coloured Salts.—The salt



is obtained in orange-red crystals by warming tetramethyldiaminotriphenylcarbinol with 30 per cent. hydrochloric acid and then adding stannic chloride. The analogous salt,



was obtained from the crystal-violet base.

Green Salts.—Under special conditions, the diacid salt,

$\text{NMe}_2\text{Cl}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2, \text{HCl}, \text{ZnCl}_2, 3\text{H}_2\text{O}$,
derived from the crystal-violet base, can be obtained in bright green crystals; it corresponds with the ordinary green salt,

$\text{NMe}_2\text{Cl}:\text{C}_6\text{H}_4:\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$,

of the malachite-green base.

W. A. D.

Replacement of the Hydroxyl Group by the Hydrazine Group. HARTWIG FRANZEN (*Ber.*, 1905, **38**, 266—270).—Two new methods of preparing hydrazines are described. α - or β -Naphthylhydrazine is formed on heating α - or β -naphthol, hydrazine sulphate, and hydrazine hydrate together with a little alcohol in a sealed tube for 8 hours at 100° . Hydrazine α - or β -hydroxynaphthoate, when heated at 140 — 150° , loses water and carbon dioxide, forming α - or β -naphthylhydrazine.

2:3-Naphthylenedihydrazine, $\text{C}_{10}\text{H}_6(\text{NH}\cdot\text{NH}_2)_2$, prepared from 2:3-dioxynaphthalene by the former method, crystallises in colourless, minute needles, melting and decomposing at 155 — 156° , which reduce Fehling's and ammoniacal silver solutions on warming; the hydrochloride forms a snow-white, crystalline mass without a sharp melting point. Benzylidene-2:3-naphthylenedihydrazone, $\text{C}_{10}\text{H}_6(\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$, crystallises from benzene in yellow needles, which melt and decompose at 205° . 1:3-Dibenzylideneamino-2-phenyl-2:3-naphthadihydroglyoxaline, $\text{C}_{10}\text{H}_6\left\langle \begin{smallmatrix} \text{N}(\text{N}\cdot\text{CHPh}) \\ \text{N}(\text{N}\cdot\text{CHPh}) \end{smallmatrix} \right\rangle \text{CHPh}$, prepared by the interaction of the hydrazine with excess of benzaldehyde, crystallises from xylene in yellow needles melting and decomposing at 227 — 228° . E. F. A.

Nitroso- and Azo-derivatives of 3-Pyrazolones. AUGUST MICHAELIS (*Ber.*, 1905, **38**, 154—155).—Substitution in all three pyrazolones is readily effected in the 4-position. Halogen derivatives are formed by the action of chlorine or of bromine on solutions of 3-pyrazolones in glacial acetic acid or chloroform.

4-Nitroso-1-phenyl-5-methyl-3-pyrazolone, $\text{NPh}\left\langle \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CMe}\cdot\text{C}\cdot\text{NO} \end{smallmatrix} \right\rangle$, prepared by the action of sodium nitrite on a solution of 1-phenyl-5-methyl-3-pyrazolone in glacial acetic acid, separates from ethyl acetate in green needles and melts indefinitely at 159° .

The azo-compound, $\text{NPh}\left\langle \begin{smallmatrix} \text{NH}\cdot\text{CO} \\ \text{CMe}\cdot\text{C}\cdot\text{N}\cdot\text{NPh} \end{smallmatrix} \right\rangle$, formed by the action of diazobenzene chloride on an alkaline solution of 1-phenyl-5-methyl-3-pyrazolone, forms gold-coloured leaflets and melts at 99 — 100° . By the action of phosphorus oxychloride, it is converted into the 3-chloropyrazole, $\text{NPh}\left\langle \begin{smallmatrix} \text{N}=\text{CCl} \\ \text{CMe}\cdot\text{C}\cdot\text{N}\cdot\text{NPh} \end{smallmatrix} \right\rangle$.

A. McK.

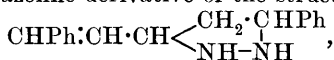
Amino-derivatives of Pyrimidine. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 149. Compare *Abstr.*, 1902, i, 59; Traube, this vol., i, 101).—As Traube states 2:4:5:6-tetraminopyrimidine to be only a di-acid base, the author has repeated the preparation and analysis of

the hydrochloride and confirms his former statement that the composition is $C_4H_8N_6, 3HCl$. G. Y.

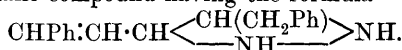
Thio-derivatives of Pyrimidine. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 156055).—Thiocarbamide and its monoalkyl derivatives react with the sodium or potassium derivative of ethyl cyanoacetate to form pyrimidine compounds of the formula $NR \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{C}(\text{SH}) : \text{N} \end{smallmatrix} > \text{C:NH}$, which are readily converted into derivatives of hypoxanthine. The compound from ethyl cyanoacetate and thiocarbamide forms colourless crystals and dissolves readily in hot water and in dilute acids or alkalis. The preparation of compounds from methylthiocarbamide and allylthiocarbamide is also described.

C. H. D.

Reduction of α -Dibenzylideneacetonehydroxylamineoxime. GAETANO MINUNNI and R. CIUSA (*Gazzetta*, 1904, 34, ii, 373—376. Compare Minunni, Abstr., 1900, i, 237; Minunni and Carta-Satta, Abstr., 1900, i, 237).—Reduction of α -dibenzylideneacetonehydroxylamineoxime with sodium and amyl alcohol yields a base, $C_{17}H_{18}N_2$, which is either a pyrazoline derivative of the structure



or a hydrazoethane compound having the formula



The hydrochloride of the base is very hygroscopic; the *platinichloride*, $C_{17}H_{18}N_2, H_2PtCl_6$, forms a yellow, crystalline powder, readily soluble in water or alcohol. The *benzoyl* derivative, $C_{17}H_{17}N_2Bz$, crystallises from alcohol in white needles melting at $209-210^\circ$.

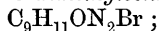
T. H. P.

Benziminazoles and their Decomposition. OTTO FISCHER (*Ber.*, 1905, 38, 320—328. Compare Abstr., 1904, i, 195).—[With O. VEIEL.]—1-Methylbenziminazole is best prepared by boiling methyl-*o*-phenylenediamine, obtained by reducing *o*-nitromethylaniline, with crystalline formic acid; it crystallises from light petroleum in white prisms, melts at 61° , and gives a *hydrochloride*, $C_8H_9N_2Cl$, crystallising from alcohol in needles; the *platinichloride*, $C_{10}H_{18}N_4PtCl_6, 2H_2O$, forms reddish-yellow prisms and the *picrate* melts at 244° .

1:3-Dibenzylbenziminazole hydrochloride, $C_{21}H_{19}N_2Cl$, obtained by heating benziminazole with benzyl chloride for several hours at 100° , crystallises from alcohol; the *platinichloride* melts at 216° , the *aurichloride* at 155° , and the *picrate* at 208° . 1:3-Dibenzylbenziminazole-2-ol, $C_{21}H_{20}ON_2$, obtained by adding potassium hydroxide to a solution of the hydrochloride, crystallises from light petroleum in colourless nodules, melts at $113-114^\circ$, and when heated with concentrated alcoholic potassium hydroxide is resolved into formic acid and *s*-dibenzyl-*o*-phenylenediamine. The latter separates from light petroleum in thick crystals, melts at 71° , and gives a *hydrochloride*, $C_{20}H_{21}N_2Cl$, melting at 149° ; it combines with salicylaldehyde to

form 2-*o*-hydroxyphenyl-1:3-dibenzylhydrobenziminazole, which crystallises from alcohol in white needles, melts at 136°, and is resolved by acids into its constituents. When *s*-dibenzyl-*o*-phenylenediamine is heated with acetic acid and a little acetic anhydride, 1:3-dibenzyl-2-methylbenziminazole-2-ol, $C_6H_4 \begin{smallmatrix} \text{N}(C_6H_5) \\ \text{N}(C_6H_5) \end{smallmatrix} > CMe \cdot OH$, is obtained, crystallising from alcohol in white needles and melting at 153°; the *platinichloride*, $C_{44}H_{42}N_4PtCl_6$, forms yellow leaflets. On oxidation with ferric chloride in alcoholic solution, the diamine is converted into *N*-tetrabenzylldiaminophenazonium chloride, $C_{40}H_{36}N_4Cl_2 \cdot 2H_2O$.

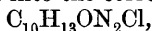
[With J. G. MOUSON.]—5-Bromobenziminazole, $C_7H_5N_2Br$, prepared by heating 4-bromo-1:2-diaminobenzene with formic acid, crystallises from water in colourless needles, melts at 137°, and gives a crystalline *platinichloride* and *aurichloride*; when heated with an excess of methyl iodide, it is converted into 5-bromo-1:3-dimethylbenziminazolium iodide $C_9H_{10}N_2BrI$, which is easily decomposed by cold aqueous sodium hydroxide, giving 5-bromo-1:3-dimethylbenziminazole-2-ol,



the latter crystallises from light petroleum in white needles, melts at 103°, and is hydrolysed by boiling aqueous sodium hydroxide to 4-bromo-*o*-phenylenedimethyldiamine; this crystallises from dilute alcohol in needles and melts at 78°.

5-Bromo-1:2:3-trimethylbenziminazolium iodide, obtained by heating 5-bromo-2-methylbenziminazole with methyl iodide, crystallises from dilute alcohol in thick, yellow prisms and is with difficulty transformed by hot aqueous potassium hydroxide into 5-bromo-1:2:3-trimethylbenziminazole-2-ol, $C_6H_3Br \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} > CMe \cdot OH$, which forms white needles and melts at 173°.

5-Chloro-1:2:3-trimethylbenziminazolium iodide, $C_{10}H_{12}N_2ClI$, prepared by the action of methyl iodide on 5-chloro-2-methylbenziminazole, is, however, converted into the corresponding *carbinol*,



by gently warming it with aqueous sodium hydroxide; the product crystallises from alcohol in colourless prisms and melts at 152–153°.

W. A. D.

Synthesis of Derivatives of Ketoquinazoline. BRONISLAW VON PAWLEWSKI (*Ber.*, 1905, 38, 130–131).—4-Keto-2-thion-3-phenyl-

1:2:3:4-tetrahydroquinazoline, $C_6H_4 \begin{smallmatrix} \text{CO-NPh} \\ \text{NH-CS} \end{smallmatrix}$, is formed when a molecular mixture of anthranilic acid and phenylthiocarbamide is heated at 160–165°. It crystallises from alcohol in small, irregular, nacreous leaflets, melts at 304–306°, and when treated with alkaline hydrogen peroxide solution is converted into 2:4-diketo-3-phenyl-

1:2:3:4-tetrahydroquinazoline, $C_6H_4 \begin{smallmatrix} \text{CO-NPh} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, which is formed also when a molecular mixture of anthranilic acid and phenylcarbamide is heated at 160–180° and finally at 200°. It crystallises in long, colourless, flat prisms and needles, from glacial acetic acid in large

leaflets, melts at 275—277°, and dissolves in aqueous alkalis to solutions which, after dilution with water, have a violet fluorescence.

G. Y.

Quinoxaline and Benziminazole Compounds from 4-Nitro-2-aminodiphenylamine. ARNOLD REISSERT and G. GOLL (*Ber.*, 1905, **38**, 90—104).—4-Nitro-2-aminodiphenylamine (Nietzki and Almenräder, *Abstr.*, 1896, i, 164) combines with potassium cyanide and formaldehyde in dilute alcoholic solution to form 5-nitro-2-anilino-phenylglycine, $\text{NHPh} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which melts at 96° after repeated precipitation from sodium carbonate solution by hydrochloric acid. It dissolves readily in alcohol, acetic acid, or acetone, sparingly in ether or benzene, but is partially dehydrated on heating, so cannot be recrystallised. On heating with concentrated sulphuric acid, water is removed and 6-nitro-2-keto-1-phenyltetrahydroquinoxaline, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \cdot \text{CH}_2 \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$, is formed; this crystallises from glacial acetic

acid in bright yellow needles when slowly cooled, or in darker yellow tablets when rapidly cooled, and melts at 230·5° after drying at 100° in a vacuum. It dissolves in concentrated acids to colourless solutions, and is not decomposed on boiling. It is insoluble in benzene or ether, but dissolves readily in hot acetone. The same compound is obtained on heating nitroaminodiphenylamine with bromoacetic acid and sodium acetate.

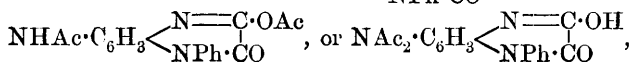
Hydrogen chloride and stannous chloride reduce the acetic acid solution to 6-amino-2-keto-1-phenyltetrahydroquinoxaline, $\text{C}_{14}\text{H}_{13}\text{ON}_3$, which crystallises from alcohol in small, colourless needles melting at 158° and becoming yellow in the air. It is insoluble in alkalis, and dissolves readily in acetone or glacial acetic acid, very sparingly in ether or benzene. Ferric chloride oxidises the hydrochloride, an intense blue coloration, rapidly becoming brown, being produced.

The diacetyl derivative, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NAc} \cdot \text{CH}_2 \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$, crystallises from dilute acetic acid in star-shaped groups of colourless, lancet-like leaflets and melts at 128—131°.

Nitroaminodiphenylamine combines with ethyl oxalate (compare Meyer and Seeliger, *Abstr.*, 1897, i, 45) on boiling to form 6-nitro-3-hydroxy-2-keto-1-phenyldihydroquinoxaline, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{N}=\text{C} \cdot \text{OH} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$,

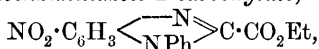
crystallising from ethyl oxalate or nitrobenzene in microscopic, colourless needles, remaining unaltered at 330°. Most organic solvents dissolve only traces. On boiling with a solution of sodium sulphide, 6-amino-3-hydroxy-2-keto-1-phenyldihydroquinoxaline, $\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_3$, is formed, and crystallises in slender, yellowish-white needles, not melting at 330°. It dissolves readily in acids or alkalis and is readily oxidised. The sulphate forms a colourless, sparingly soluble precipitate.

The diacetyl derivative, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NAc} \cdot \text{CO} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$,



forms small, colourless crystals, infusible at 300° , and dissolves readily in alkalis, thus suggesting the third of the above formulæ.

In the condensation of nitroaminodiphenylamine with ethyl oxalate, *ethyl 5-nitro-1-phenylbenziminazole-2-carboxylate*,

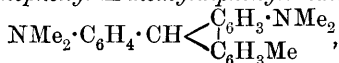


is also produced, which crystallises from alcohol in colourless, tabular leaflets and melts at 150.5° . It dissolves readily in chloroform or hot acetic acid, acetone, or ethyl oxalate, sparingly in ether or benzene. The *carboxylic acid* forms a colourless, uncrystallisable powder, dissolving readily in alcohol, acetic acid, or acetone, sparingly in ether or benzene, and does not melt at 300° .

Concentrated hydrochloric acid decomposes the ester at 150° , forming *5-nitro-1-phenylbenziminazole*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NPh} \end{array} \text{CH}$, which forms colourless crystals and melts at 159.5° and dissolves readily in acids. Stannous chloride reduces it to *5-amino-1-phenylbenziminazole*, $\text{C}_{13}\text{H}_{11}\text{N}_3$, separating from benzene in colourless crystals and melting at $130\text{--}131^{\circ}$. The *stannochloride*, $\text{C}_{13}\text{H}_{11}\text{N}_3 \cdot 2\text{HCl} \cdot \text{SnCl}_2$, forms colourless needles. The *acetyl* derivative, $\text{C}_{15}\text{H}_{13}\text{ON}_3$, forms small, colourless crystals melting at 170.5° and yields a crystalline *hydrochloride*.
C. H. D.

Amino-derivatives of Phenyldiphenylenemethane and the Corresponding Carbinol. ALFRED GUYOT and M. GRANDERYE (*Bull. Soc. chim.*, 1905, [iii], 33, 198—205. Compare Abstr., 1901, i, 569; 1903, i, 748, and Ullmann and Wursterberger, Abstr., 1904, i, 154).—*as-Tetramethyldiaminophenyldiphenylenemethane*, produced together with the *o*-hydroxy-leuco-base of malachite-green (Fischer, Abstr., 1881, 587) by diazotising the *o*-amino-leuco-base of malachite-green in sulphuric acid and then heating at 100° , melts at 158° (compare Abstr., 1903, i, 748).

Tetramethyldiaminophenyl-m-methyldiphenylenemethane,



similarly prepared from Noeltling's base (Abstr., 1891, 727, and 1892, 187), having the constitution $\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ by diazotisation, forms small, white crystals, melts at 142° , and is slightly soluble in alcohol and ether, more so in benzene. On oxidation, it furnishes a dull violet dye. *Tetramethyldiaminophenyl-m-nitrodiphenylenemethane*, similarly prepared from a *nitro*-base which will be described in a future paper, crystallises in slender, brilliant, orange-yellow needles, melts at 170° , resembles the foregoing in solubility, and gives a blue dye on oxidation.

Tetramethyldiaminophenylphenylenenaphthylenemethane, similarly prepared from the *base* $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \\ \diagup \quad \diagdown \\ \text{C}_{10}\text{H}_6 \cdot \text{NH}_2 \end{array}$, to be described in a future paper, forms slender, white needles, melts at $225\text{--}226^{\circ}$, and is soluble in benzene and scarcely so in alcohol and ether. T. A. H.

Desmotropic Compounds. HEINRICH GOLDSCHMIDT (*Zeit. Elektrochem.*, 1905, 11, 5—7).—Dimroth (this vol., i, 98), from his experiments on the velocity of the conversion of methyl 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate into its ketonic form, has drawn the conclusion that the reaction only affects the non-dissociated molecules and does not take place between the ions. Owing to the fact that the non-dissociated molecules are in equilibrium with the ions, however, the product of the concentrations of the ions is proportional to the concentration of the non-dissociated molecules, and the velocity of reaction, which Dimroth has shown to be proportional to the latter, is therefore proportional to the former. Hence the experiments cannot decide whether the change is ionic or not. T. E.

[2:2'-Diamino-4:4'-oxalotoluidide.] FARBERWERKE VORM. MEISTER LUCIUS, & BRÜNING (D.R.-P. 156177).—*m*-Tolylenediamine combines with oxalic acid at 100—225° to form 2:2'-diamino-4:4'-oxalotoluidide, $C_2O_2(NH \cdot C_6H_3Me \cdot NH_2)_2$, which separates as an amorphous, yellow powder melting at 180—220°, according to the mode of precipitation. It is insoluble in water and dissolves sparingly in hot alcohol to a yellow solution with slight green fluorescence. Azo-dyes may be prepared from the tetrazonium compound.

On fusing diamino-oxalotoluidide with sulphur at 80—140°, hydrogen sulphide is evolved and the reaction then ceases, but on heating further, condensation takes place at 170° and a new compound is obtained, which dyes a fast yellow shade in a sodium sulphide bath.

C. H. D.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. XVIII. **Action of Ammonia on Tetrabromobenzylidenazine.** ROBERT STOLLÉ (*J. pr. Chem.*, 1905, [ii], 71, 30—33. Compare Abstr., 1903, i, 721; 1904, i, 102, 200, 453, 626, 627, 694—697; this vol., i, 94—97).—The action of ammonia on a cooled solution of tetrabromobenzylidenazine in carbon tetrachloride leads to the formation of a benzylidene derivative of 3:6-diphenyl-1:4-dihydropyridazine and benzylidenazine.

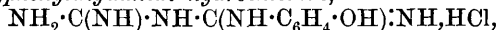
The *benzylidene* derivative, $N \begin{array}{c} \diagup \text{CPh:N} \\ \diagdown \text{CHPh} \\ \diagup \text{N:CPh} \end{array} N$, is formed also when

3:6-diphenyl-1:4-dihydropyridazine is shaken with benzaldehyde and dilute sulphuric acid. It crystallises in needles, melts at 207°, is soluble in alcohol or carbon tetrachloride, but not in water, and yields the dihydropyridazine when a current of steam is passed through a suspension of it in dilute sulphuric acid. G. Y.

Action of Dicyanodiamide on the Primary Aromatic Amine Hydrochlorides. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1905, [iii], 33, 205—207).—The authors find that in the preparation of phenyldiguanides by the action of dicyanodiamide (cyanoguanidine) on aniline hydrochloride, it is unnecessary to heat the reagents, dissolved in alcohol, in closed vessels, since

the reaction takes place when the two reagents are fused together over an oil-bath (compare Smolka and Friedrich, Abstr., 1888, 830).

p-Hydroxyphenyldiguanide hydrochloride,



similarly prepared, melts at 203—204°; the *picrate* melts at 200—201°. *p*-Anisyldiguanide hydrochloride melts at 221—222° and the *picrate* at 193—195°.

The *o*- and *p*-phenetyldiguanide hydrochlorides melt respectively at 183—184° and 209—210°, and the corresponding *picrates* at 161—162° and 182—183° respectively. The *diguanide* derived from antipyrine yields a *picrate* melting and decomposing at 137—138°. These hydrochlorides, on treatment with silver oxide, furnish the *diguanides*, which are strongly alkaline substances, very soluble in water. T. A. H.

[*o*-Hydroxyazo-derivatives of α -Naphthylamine.] BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 156440).—Whilst it is not possible to substitute hydroxyl for the sulpho-group in diazobenzene-*o*-sulphonic acid and its homologues by means of alkaline compounds, the reaction takes place readily in the case of the di- and poly-sulphonic acids of α -naphthylamine. The diazo-compounds of α -naphthylamine-2:4- and -2:5-disulphonic acids, or of α -naphthylamine-2:4:6- or -2:4:7-trisulphonic acids, react in the cold with alkali or alkaline earth acetates or carbonates, or with alkali nitrites, the sulpho-group being replaced by hydroxyl. The diazohydroxy-compounds thus obtained do not combine readily, but yield stable brown or violet dyes with β -naphthol. Subsequent treatment with chromium salts produces fast dark blue or black shades. C. H. D.

Limits of Coupling of Diazobenzene with Aniline. LÉO VIGNON (*Compt. rend.*, 1905, 140, 91—93. Compare Abstr., 1904, i, 637, 1065).—Diazobenzene chloride does not condense with aminoazobenzene either in aqueous or alcoholic solution, but aniline condenses readily with diazoaminoazobenzene at 0° to form the compound $\text{NPh} : \text{N} \cdot \text{C}_6\text{H}_4 : \text{N} : \text{N} \cdot \text{NHPh}$, which crystallises from alcohol, melts at 112°, and on prolonged heating at 40° with aniline and aniline hydrochloride breaks down into aminoazobenzene (compare, however, Nietzki and Diesterweg, Abstr., 1888, 1080). Anilinebisdiazobenzene, $\text{NH}(\text{N} : \text{NPh})_2$, prepared by the action of aniline on nitrosoacetanilide (Pechmann and Frobenius, Abstr., 1894, i, 283), when heated with aniline and aniline hydrochloride also yields aminoazobenzene, which appears to represent the limit of combination of diazobenzene with aniline (compare Abstr., 1904, i, 701). Attempts to prepare anilinebisdiazobenzene by the action of diazobenzene chloride on diazoaminobenzene or on aniline were unsuccessful. M. A. W.

[**Azo-dyes from Alkylsulphonaminonaphthol Derivatives.**] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156157).—Benzenesulphonic chloride reacts with 8-amino- α -naphthol-4-sulphonic acid in alkaline solution to form 8-benzenesulphonamino- α -naphthol-4-sulphonic acid, which is sparingly soluble. The quantity present may be determined by titration with a nitrophenyldiazonium salt in acetic acid

solution. The acid combines with diazotised picramic acid in slightly alkaline solution to form a crystalline *azo*-compound, which may be filtered, washed with sodium chloride solution, and dried. The dye dissolves in water to a violet solution, becoming red on the addition of alkalis. It yields fast bluish-black shades on subsequent treatment with chromium salts. Similar compounds are obtained from *o*- or *p*-toluenesulphonic chloride.

C. H. D.

[**Azo-dyes from Nitro-*m*-diamines.**] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156352).—The diazosulphonic acids of the benzene and naphthalene series, such as the diazo-compounds of *p*-toluidine-*o*-sulphonic, *p*-chloroaniline-*m*-sulphonic, or β -naphthylamine-8-sulphonic acid, combine with nitrated *m*-diamines to form monoazo-dyes, which yield fast yellow or orange lakes with metallic salts.

C. H. D.

Protective Action of Salt on Solutions of Proteids. WILHELM BILTZ (*Zeit. Elektrochem.*, 1904, 10, 937—938).—Precipitated and well-washed hydrated ferric oxide or zirconium dioxide was shaken with solutions containing albumin and the quantity of albumin remaining in solution determined. A comparison of the results obtained with solutions containing salt and with dialysed solutions showed that the latter lost more albumin than the former. It is probable that a maximum protective action would be found at a certain concentration of salt, since a large excess of it precipitates albumin. The observations give an explanation of the fact that circulating blood does not coagulate.

T. E.

Action of Pepsin on Albumin Precipitated by Heat in Presence of Acid. F. DISDIER (*J. Pharm. Chim.*, 1905, [vi], 21, 5—14).—The amount of acetic, tartaric, and oxalic acids in one per cent. solutions required for the precipitation of 100 grams of white of egg are 45, 57, and 48 c.c. respectively, numbers which are directly proportional to the equivalent weights of the acids. This rule also holds with nitric, butyric, and citric acids.

Using the most favourable proportions of hydrochloric acid for the digestion by pepsin of albumin precipitated by acid and for dissolved albumin, the author finds that, whilst the rates of digestion are equal with an acidity of 0.2 per cent., with an acidity of 0.1 per cent., 9 grams of precipitated albumin require 3 hours, the same weight of dissolved material requiring 12 hours for digestion. The difference in the acidity necessary for digestion is not due to acid combined with the precipitated albumin.

G. D. L.

Oxidation of Proteids with Calcium Permanganate. II. Oxidation of Gelatin. FRIEDRICH KUTSCHER and MARTIN SCHENCK (*Ber.*, 1905, 38, 455—459. Compare Abstr., 1904, i, 955).—The crystalline product obtained in the oxidation of gelatin with calcium permanganate, and formerly described as oxaluramide, proves to be oxamide. The filtrate contains guanidine in quantity corresponding with the arginine in the original material (compare also Loew, Abstr., 1885, 823).

C. H. D.

Hydrolytic Cleavage of Proto-albumose. PHOEBUS A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1904, xii—xiii; *Amer. J. Physiol.*, 13).—Mixed with the hexone bases obtained from proto-albumose, a new material, $C_{12}H_{22}O_5N_4$, was obtained. The copper and silver salts were prepared and analysed; further investigation is in progress.

W. D. H.

Haloid Acid Salts of Peptones. KALLE & Co. (D.R.-P. 156399).—The irritant compounds produced in the action of haloid acids on peptones may be removed by washing the products with an alkali carbonate solution until neutral. The pure peptone salts yield non-irritant double salts with metallic haloids.

C. H. D.

Protagon. E. R. POSNER and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1904, xxxv; *Amer. J. Physiol.*, 13).—Further facts in favour of the view that protagon is not a chemical unit.

W. D. H.

Absorptiometric Estimation of the Amount of Nitric Oxide combined by Unit Weight of Methæmoglobin. GUSTAV VON HÜFNER and B. REINOLD (*Chem. Centr.*, 1905, i, 374; from *Arch. Anat. Physiol., physiol. Abth.*, 1904, 391—395).—Methæmoglobin solutions take a purplish-red colour with nitric oxide (Hüfner and Otto); Hüfner and Külz state that the spectroscopic appearances of such a solution are the same as those of a solution obtained by passing a stream of nitric oxide through a solution of carboxyhæmoglobin. It is now shown that the volume of nitric oxide per gram of pigment is almost twice as great as that of carbon monoxide united to each gram of hæmoglobin.

W. D. H.

Hæmochromogen and Carbon Monoxide. GUSTAV VON HÜFNER and WILLIAM KÜSTER (*Chem. Centr.*, 1905, i, 373—374; from *Arch. Anat. Physiol., physiol. Abth.*, 1904, 387—390).—Hæmochromogen was prepared from aceto-hæmin by reduction with potassium hydrosulphide; this combines with carbon monoxide, like hæmoglobin, in the proportion of 1 molecule of the gas per atom of iron.

W. D. H.

Spectroscopic Characters of Hæmatoporphyrin. ARTHUR SCHULZ (*Chem. Centr.*, 1905, i, 373; from *Arch. Anat. Physiol., physiol. Abth.*, 1904, 271—286).—Hæmatoporphyrin, prepared by Nencki and Zaleski's methods, dissolved in alcohol shows five spectroscopic bands; the positions and relative intensities of these are described, as also are the changes which occur in them with different concentrations, or on the addition of such reagents as acids, alkalis, and zinc chloride.

W. D. H.

Organic Chemistry.

Some Constants of Pure Methane. The Action of Solid Methane on Liquid Fluorine. HENRI MOISSAN and G. CHAVANNE (*Compt. rend.*, 1905, 140, 407—410).—Pure methane, prepared by the action of water on aluminium carbide (compare Abstr., 1894, ii, 450) in a vessel from which all air had been removed, and purified by liquefying and then solidifying in a vacuum (compare Abstr., 1903, ii, 642), has a sweet and slightly alliaceous odour, a density 0.5540 to 0.5554 at 0° and under 760 mm. pressure; Thomson gives 0.558, and Schloesing 0.558 (compare Abstr., 1896, i, 401); it solidifies to a colourless, transparent, vitreous mass at the temperature of liquid air, and after a few moments crystallises in white needles, melting at -184° to a colourless liquid boiling at -164° under 760 mm. pressure; Olszewski gives -185.8° and -164° for the same constants (compare Abstr., 1885, 860).

When a closed tube containing solid methane is opened under liquid fluorine at -187°, there is a violent explosion accompanied by incandescence, the glass vessels being reduced to powder. The energy of the reaction is comparable with that which occurs between solid fluorine and liquid hydrogen (compare Abstr., 1903, ii, 360), and affords a further instance of the persistency of chemical affinity at very low temperatures. M. A. W.

Light Petroleum, Vaseline Oil, and Vaseline. PAUL ADAMS (*Bull. Soc. chim.*, 1905, [iii], 33, 274—283).—The author asserts that much of the light petroleum of commerce consists of the liquid hydrocarbons produced by "cracking" petroleum residues. A number of samples of light petroleum prepared about 1897 by the distillation of crude petroleum were examined. They absorbed quantities of bromine varying from 10 to 140 per cent. by weight, and lost this property after treatment with sulphuric acid. A crude light petroleum obtained by "cracking" petroleum residues, distilled between 60° and 135°, had a sp. gr. 0.712, absorbed 60 per cent. by weight of bromine, and when shaken with sulphuric acid, 21.15 per cent. was dissolved and the acid became black. A crude light petroleum obtained by fractional distillation of crude petroleum without "cracking" possessed a slight yellow colour, was dichroic, distilled between 40° and 130°, had a sp. gr. 0.675, absorbed 0.6 per cent. of its weight of bromine, forming a white precipitate and evolving hydrogen bromide. Sulphuric acid decolorised the material and itself became brown. A specimen of "gasolin," prepared from the foregoing by washing first with sulphuric acid and then with a solution of sodium hydroxide, distilled between 30° and 85°, had a sp. gr. 0.64, and did not react with mercury hydrogen sulphate or immediately with bromine in the cold.

A sample of vaselin oil, distilled unchanged between 335° and 440°, did not react with bromine in the cold and was not sensibly diminished in volume by agitation with sulphuric acid.

Vaselin should consist of the decolorised and deodorised residue of American petroleum after distilling off all products volatile below 360° , with the addition of from 2 to 5 per cent. of hard paraffin. On distillation, the constituents of vaselin undergo decomposition, and the products are crystalline paraffins, liquid hydrocarbons, and small quantities of gas, the two latter being partially ethylenic (compare Engler, *Abstr.*, 1898, i, 165). The hard paraffin slowly separates when the distillate is kept. The author concludes that no hard paraffin exists already formed in vaselin. A list of the requirements to which vaselin should conform is given in the original. T. A. H.

Reaction distinguishing between Primary, Secondary, and Tertiary Alcohols. PAUL SABATIER and JEAN B. SENDERENS (*Bull. Soc. chim.*, 1905, [iii], 33, 263—264. Compare *Abstr.*, 1903, i, 393, 453, 454).—The authors utilise the characteristic products obtained from these different classes of alcohols as the result of their catalytic decomposition by metallic copper at 300° to distinguish between them, and an apparatus suitable for this purpose is described. The aldehydes produced under these conditions from primary alcohols are detected by means of magenta decolorised with sulphurous acid; the ketones obtained from secondary alcohols, by the formation of a precipitate with a solution of semicarbazide hydrochloride in presence of potassium acetate; and the liquid olefinic hydrocarbons furnished by tertiary alcohols (except trimethylcarbinol, which yields a gas), by their property of immediately decolorising bromine. T. A. H.

Fusibility in the Series of Normal Di-primary Glycols. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1904, 1142—1149).—It is shown that so far as fusibility, as measured by melting point, is concerned this series consists of two partial series constituted by (a) those terms having an even number of carbon atoms, and (b) those having an odd number of carbon atoms. The data for the first of these partial series is fairly complete, and in this fusibility diminishes as the series is ascended. The differences between the melting points of consecutive pairs from C_2 to C_8 are 28° , 24° , and 23° respectively, and between C_8 and C_{10} , 8° . T. A. H.

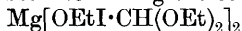
Solubility of Metallic Hydroxides in Glycerol. ARTHUR MÜLLER (*Zeit. anorg. Chem.*, 1905, 43, 320—325).—Definite weights of glucinum nitrate, aluminium nitrate, chrome alum, ferrous ammonium sulphate, ferric chloride, ceric ammonium nitrate, cerous ammonium nitrate, and neodymium magnesium nitrate respectively were dissolved in water, mixed with glycerol, and then agitated after the addition of ammonia. The behaviour of the resulting solutions on heating and on dilution with water is recorded. Glucinum and ceric hydroxides were insoluble, aluminium and chromium hydroxides sparingly soluble, and the other hydroxides easily soluble under the conditions used. A. McK.

Basic Properties and the Quadrivalence of Oxygen. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1905, 27, 26—29).—Archibald and

McIntosh (Trans., 1904, 85, 919) have shown that in certain compounds of the ethers and alcohols with hydrogen chloride the valency of the oxygen may be assumed to be as high as twelve. In view of this result, compounds of methyl ether and methyl alcohol with hydrogen bromide and hydrogen iodide have been prepared. These compounds are white, crystalline solids, almost insoluble in the ether or alcohol, but readily soluble in the liquefied acid used in their preparation; their formation is accompanied by the development of a large amount of heat. The compound $(\text{CH}_3)_2\text{O} \cdot \text{HI}$ melts at -15° , the compound $\text{CH}_3 \cdot \text{OH} \cdot \text{HI}$ at -48° , the compound $(\text{CH}_3)_2\text{O} \cdot \text{HBr}$ at -22° , and the compound $\text{CH}_3 \cdot \text{OH} \cdot \text{HBr}$ at -14° . In all these cases the oxygen is quadrivalent, and hence the experiments afford no further evidence as to the possibility of oxygen existing with a valency of eight or twelve. E. G.

Quadrivalent Oxygen. EDMOND E. BLAISE (*Compt. rend.*, 1905, 140, 661—663. Compare this vol., ii, 111).—By the action of zinc on iodine in presence of ethyl ether, a crystalline compound of the formula $\text{Zn}(\text{OEt}_2\text{I})_2$ is obtained. It is less stable than the corresponding magnesium compound (*loc. cit.*), but reacts with benzoyl chloride in a similar manner, giving rise to ethyl iodide, ethyl benzoate, and zinc chloride. When the diethyl ether groups in this compound are replaced by methyl amyl ether, the products of the reaction with benzoyl chloride are methyl iodide and amyl benzoate. The group with the smaller number of carbon atoms thus enters into combination with the iodine. If one of the ether groups is cyclic and has one of the carbon atoms attached directly to the oxygen atom, the reaction with benzoyl chloride is different. Hydrogen chloride is produced and the benzoyl group enters into combination with one of the carbon atoms of the nucleus.

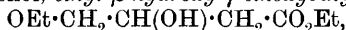
Acetals give rise to analogous zinc iodine compounds and these react with benzoyl chloride in a similar manner. When ethyl orthoformate is added in small portions at a time to an ethereal solution of the compound $\text{Hg}(\text{OEt}_2\text{I})_2$, a substance having the constitution



separates in well-formed crystals. It reacts energetically with benzoyl chloride, the products being ethyl iodide, formate, and benzoate. The compounds which the ethers, acetals, and ortho-esters form with iodine and magnesium (or zinc) are thus all of the same type. Their properties and behaviour towards benzoyl chloride indicate the presence of quadrivalent oxygen atoms. The compounds which the esters form with iodine and magnesium are of a different type, $(\text{RCO}_2\text{R}')_6\text{MgI}_2$, and behave differently towards benzoyl chloride. H. M. D.

Action of Hydrogen Cyanide on Epiethylin (Ethyl Glycide Ether). ROBERT LESPIEAU (*Compt. rend.*, 1905, 140, 436—437).—Bromoethylin (α -bromoethoxyhydrin), obtained by the action of phosphorous bromide on glycerol α -monoethyl ether, boils at 197° under 760 mm. pressure and reacts with potassium hydroxide to form epiethylin (ethyl

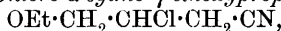
glycide ether), $O \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{OEt} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}$, which combines with hydrogen cyanide, slowly at the ordinary temperature, or more rapidly at 70° , to form α -cyano- β -hydroxy- γ -ethoxypropane, $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CN}$, a colourless liquid, soluble in water, boiling at $243\text{--}245^\circ$ under 760° mm. pressure, and yielding, on saponification with hydrochloric acid in the presence of alcohol, *ethyl β -hydroxy- γ -ethoxybutyric acid*,



boiling at $120\text{--}121^\circ$ under 13 mm. pressure, and converted by the action of potassium hydroxide into the potassium salt of the corresponding acid, *β -hydroxy- γ -ethoxybutyric acid*,



which is a syrup and loses 1 mol. H_2O on distillation, forming an unsaturated acid. *β -Chloro- α -cyano- γ -ethoxypropane*,



obtained by the action of phosphorus pentachloride on the corresponding hydroxy-compound, boils at 105° under 19 mm. pressure, from which *β -chloro- γ -ethoxybutyric acid*, $\text{OEt} \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, boiling at $144\text{--}145^\circ$ under 14 mm. pressure and melting at 2° , and its *amide*, melting at 64° , are readily obtained by the ordinary methods.

M. A. W.

Preparation of Nitro-products of Organic Compounds.

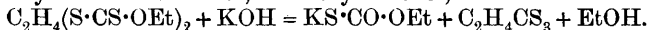
J. MATUSCHEK (*Chem. Zeit.*, 1905, 29, 115).—Ethyl nitrite is formed by the action of sodium nitrite on magnesium sulphate in presence of ethyl alcohol, since magnesium nitrite is unstable, especially when its solution is heated. The change $\text{Mg}(\text{NO}_2)_2 + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{NO}_2 + \text{NO}$ is undergone, whilst the nitrogen peroxide thus formed acts on the ethyl alcohol present. A similar result was obtained with iron salts.

Phenols, amines, and aldehydes may be nitrated in a similar manner, the solvent used in these cases being ether.

Nitrobenzene is formed when a little ferric chloride is added to a mixture of powdered sodium nitrite and benzene.

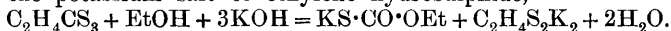
A. McK

Ethylene Xanthate and Ethylene Thiocarbonate. P. FRASSETTI (*Ber.*, 1905, 38, 488—492. Compare Welde, *J. pr. Chem.*, 1877, [ii], 15, 55).—Alcoholic potash converts ethylene xanthate into Bender's salt, ethylene thiocarbonate, and ethyl alcohol,



The yield of ethylene thiocarbonate is theoretical when only one equivalent of alkali is employed. It crystallises from a mixture of alcohol and ether in pale yellow, rhombic needles melting at 39° . Ethylene disulphide is obtained when the alcoholic filtrate from Bender's salt is exposed to the air, and on reduction with sodium amalgam it is converted into the sodium salt of ethylene hydrosulphide, $\text{C}_2\text{H}_4(\text{SNa})_2$. An ethereal solution of ethyl xanthate reacts with alcoholic ammonia, yielding xanthamide and ethylene thiocarbonate.

Ethylene thiocarbonate and alcoholic potash yield Bender's salt and the potassium salt of ethylene hydrosulphide,



J. J. S.

The Non-existence of Two Stereoisomerides of Ethyl $\alpha\beta$ -Dioximidobutyrate. LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1905, 140, 438—440; *Ber.*, 1904, 38, 926—931).—Ethyl $\alpha\beta$ -dioximidobutyrate, obtained by the action of hydroxylamine hydrochloride on ethyl diketobutyrate (compare Abstr., 1904, i, 556), crystallises from ether and light petroleum in large, transparent crystals melting at 160—162°, and the same compound is obtained, together with isonitrosomethylisooxazolone, melting at 159°, when pure ethyl isonitrosoacetate reacts with hydroxylamine in acid or alkaline solution. Ethyl $\alpha\beta$ -dioximidobutyrate is partially converted to isonitrosomethylisooxazolone by the action of hydrogen chloride in ethereal solution, but the two constituents of the solid mixture are readily separated by the action of water, which dissolves the isooxazolone, but not the dioxime.

The *mono-acetyl* derivative of ethyl $\alpha\beta$ -dioximidobutyrate, prepared by the action of acetyl chloride on the dioxime, melts at 149°, and the *diacetyl* derivative prepared by the action of acetic anhydride on the dioxime or the mono-acetyl derivative melts at 53—54°.

From these results, the author concludes that there is only one ethyl $\alpha\beta$ -dioximidobutyrate, the *syn*- and *amphi*-stereoisomerides melting at 142° and 132° respectively, described by Nussberger (Abstr., 1892, 1175), and the compound melting at 140°, described by Cérésle and Köckert (Abstr., 1884, 1120), being mixtures of the dioxime and the isooxazolone, whilst the *amphi*-diacetyl derivative melting at 119—120°, described by Nussberger, was probably an impure mono-acetyl derivative.
M. A. W.

Marckwald's Asymmetric Synthesis of Optically Active Valeric Acid. S. TIJMSTRA (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 465—468).—Methylethylmalonic acid may be converted into valeric acid [α -methylbutyric acid] at 100° at the ordinary pressure if the carbon dioxide eliminated is removed from the sphere of action.

The author modifies Marckwald's asymmetric synthesis (Abstr., 1904, i, 221) by heating the hydrogen brucine salt of methylethylmalonic acid with continual evacuation at 120° instead of heating at the melting point, 155°, as Marckwald did. In this way, the racemisation phenomena, supposed by Marckwald to occur under the conditions employed by him, are less marked. The valeric [α -methylbutyric] acid obtained had $[\alpha]_D -4.3^\circ$, which corresponds with 25.8 per cent. of *L*-valeric acid, whereas Marckwald's product had $\alpha_D -1.7^\circ$ ($l = 1$), which corresponds with about 10 per cent. of *L*-acid.
A. McK.

Direct Fixation of Organo-magnesium Derivatives on the Ethylenic Linking of Unsaturated Esters. EDMOND E. BLAISE and A. COURTOT (*Compt. rend.*, 1905, 140, 370—372).—Ethyl methylacrylate, readily prepared by the action of diethylaniline on ethyl α -bromoisobutyrate, reacts with magnesium methyl iodide at 0° to form a condensation product, which, on decomposition with water, yields a mixture of dimethylpropenylcarbinol (compare Chupotsky and Mariutza, Abstr., 1890, 727) boiling at 119° and γ -methylpentane- β -one

boiling at 116° , having an agreeable odour similar to that of camphor, and forming an oxime boiling at 89° under 20 mm. pressure, a phenyl hydrazone boiling at 153° under 10 mm. pressure, and a crystalline semicarbazone melting at 96° and identical with the ketone obtained synthetically by the hydrolysis of ethyl methylethylacetoacetate. Magnesium ethyl iodide reacts with ethyl methylacrylate, but the sole product of the reaction is diethylpropenylcarbinol, boiling at 162° , whilst magnesium methyl iodide and ethyl $\alpha\alpha$ -dimethylacrylate yield dimethylisobutenylcarbinol boiling at 138° , $\beta\delta$ -dimethyl- Δ^{γ} -pentadiene boiling at 90° , and a small quantity of a ketone, probably $\beta\beta$ -dimethylpentane- δ -one, yielding a semicarbazone melting at 124° . M. A. W.

Influence of Atmospheric Moisture on the Oxygen Absorption of Oils. III. WALTER LIPPERT (*Zeit. angew. Chem.*, 1905, 18, 94—95).—Various oils examined dried more quickly in a dry atmosphere than in a moist one. When traces of manganese are present, the oil dries better in a moist atmosphere than in a dry one.

A. McK.

Mechanism of the Ethyl Acetoacetate Syntheses. LUDWIG CLAISEN (*Ber.*, 1905, 38, 709—719).—A theoretical paper, discussing the fact that in preparing ethyl acetoacetate a better yield is obtained by using metallic sodium than by means of sodium ethoxide (compare Michael, *Abstr.*, 1901, i, 123).

W. A. D.

Lactone of Triacetic Acid. ANTONIO TAMBURELLO (*Chem. Centr.*, 1905, i, 348; privately printed, Palermo, July 1904).—The results recorded agree with the observations of Dieckmann and Breest (*Abstr.*, 1904, i, 846).

The formation of mono- and tri-phenylhydrazones agrees with a ketonic structure for the lactone, $O \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CMe}:\text{CH} \end{smallmatrix} > \text{CO}$, the inactivity of the phenylhydrazone towards *o*-phenylenediamine showing that the two carbonyl groups are not in the ortho-position. The acidity, formation of salts, red colour reaction with ferric chloride, and formation of *O*-ethers by means of diazo-methane or -ethane, or from ethyl iodide and the silver salt, agree with the desmotropic structure, $O \begin{smallmatrix} \text{C}(\text{OH}):\text{CH} \\ \text{CMe}=\text{CH} \end{smallmatrix} > \text{CO}$. The monobromo-derivative resembles the lactone, and like it must contain an unaltered methylene group and be either $O \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CMe}:\text{CBr} \end{smallmatrix} > \text{CO}$ or $O \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{C}(\text{CH}_2\text{Br}):\text{CH} \end{smallmatrix} > \text{CO}$.

The *phenylhydrazone*, $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_2$, prepared by means of diazobenzene acetate, forms red needles from alcohol or benzene, melts at 185 — 186° , and with phenylhydrazone (2 mols.) yields the *triphenylhydrazone*, $\text{C}_6\text{H}_4\text{O}(\text{N}_2\text{HPh})_3$, which forms yellow leaflets from alcohol or benzene, melts at 174 — 175° , and gives the osotetrazone reaction with ferric chloride. Nitrous vapours form, with a cold ethereal suspension of the lactone, a *nitro*-compound, $\text{C}_6\text{H}_5\text{O}_3\cdot\text{ON}\cdot\text{C}_6\text{H}_5\text{O}_3\text{NO}_2$, which forms needles decomposing explosively at 165 — 166° .

Diazomethane produces the *O-methyl ether*, which forms needles soluble in cold alcohol or ether and melts at $81-82^{\circ}$; the *ethyl ether*, prepared in similar manner or from the silver salt and ethyl iodide, melts at $59-60^{\circ}$. With diazomethane, the monobromolactone gives the *O-methyl ether*, which crystallises from benzene in plates, melts at $153-154^{\circ}$, and gives no coloration with ferric chloride. G. D. L.

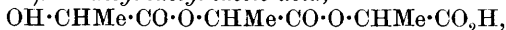
Variations in the Crystallisation of Potassium Hydrogen Succinate due to the Presence of Other Metallic Compounds in the Solution. ALEXANDER T. CAMERON (*Proc. Roy. Soc. Edin.*, 1905, 25, 449—451).—From a solution obtained by boiling potassium hydrogen succinate with freshly precipitated chromic hydroxide, crystals of potassium hydrogen succinate and, later, a green, crystalline powder are deposited. On concentrating to about half the volume and keeping, dark green crystals having the form of oblique elliptical double cones possessing monoclinic symmetry are obtained. The percentage of chromium in different preparations varies considerably, but is always less than 1 per cent. Since potassium hydrogen succinate crystallises in monoclinic crystals, the author suspects that the green crystals represent potassium hydrogen succinate containing some chromium compound, possibly in solid solution, this bringing about a modification in the external surfaces of the crystals. Similar crystals with curved faces have been obtained from solutions of the succinate after treatment with aluminium hydroxide, ferric chloride, or copper carbonate.

Chromic hydroxide dissolves readily in potassium hydrogen malate, and the solution deposits crystals similar to the above. H. M. D.

Methyl Itaconate. RICHARD ANSCHÜTZ [and FERDINAND HAAS] (*Ber.*, 1905, 38, 690—693).—Methyl itaconate has hitherto only been obtained as a liquid which slowly undergoes polymerisation; when prepared from pure silver itaconate and methyl iodide, it readily solidifies, and, after recrystallisation from methyl alcohol, melts at 38° and boils at 108° under 11 mm. or at 208° under 760 mm. pressure. It forms monoclinic crystals [$a : b : c = 1.7372 : 1 : 1.0094$; $\beta = 100^{\circ}24'$], has a normal molecular weight in ethereal solution and in the state of vapour, and does not polymerise after several months.

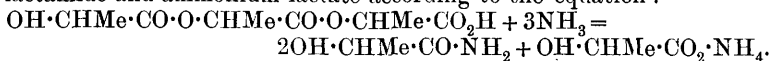
W. A. D.

Lactyl-lactyl-lactic Acid and the Dilactide of Inactive Lactic Acid. EMIL JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1905, 140, 502—505).—*Lactyl-lactyl-lactic acid*,



obtained together with dilactide when lactic acid is distilled at $230-250^{\circ}$ under 25 mm. pressure, is much more readily soluble in ether than the dilactide, crystallising in tufts of small, colourless needles melting at 39° and boiling at $235-240^{\circ}$ under 20 mm. pressure, and readily soluble in chloroform, benzene, or acetic acid. It dissolves readily in water, and the aqueous solution is hydrolysed slowly at the ordinary temperature or rapidly at 100° , forming 3 mols.

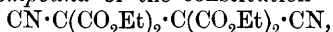
of lactic acid ; by the action of gaseous ammonia, it is decomposed into lactamide and ammonium lactate according to the equation :



The hydrolysis of racemic dilactide to lactic acid occurs through the intermediate formation of lactyl-lactic acid, and this explains the slow deposition of zinc lactate from a solution of dilactide neutralised by zinc oxide observed by Wislicenus ; the solution contained zinc lactyl-lactate, which was slowly hydrolysed into lactic acid and zinc lactate.

M. A. W.

Electro-synthesis among the Cyano-derivatives. CELSO ULPANI and G. A. RODANO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 110—114).—Electrolysis of an aqueous solution of ethyl sodiocyanomalonate yields a *compound* of the constitution



which separates from aqueous alcohol in white crystals (+ $1\frac{1}{2}\text{H}_2\text{O}$) melting at 56—57° and is readily soluble in alcohol, ether, chloroform, or benzene. It has the normal molecular weight in freezing benzene. The best yield is obtained with a 1 per cent. solution of the sodium salt of ethyl cyanomalonate and a current intensity of 0.2—0.25 amperes.

T. H. P.

Formaldehyde Sodium Hydrogen Hyposulphite. LUC. BAUMANN, GEORGES THESMAR, and JOS. FROSSARD (*Bull. Soc. Ind. Mulhouse*, 1904, 74, 348—360. Compare Prud'homme, this vol., ii, 157).—Zinc dust and sulphuric acid are added to a mixture of sodium hydrogen sulphite and ice. The zinc is then removed by the addition of sodium hydrogen carbonate, and from the filtrate so-called "sodium hyposulphite" is precipitated by the addition of brine (compare Bernthsen and Bazlen Abstr., 1900, ii, 203). A solution of this in 40 per cent. formaldehyde, when cooled, deposits a crystalline product having a composition approximately represented by the formula $\text{Na}_2\text{S}_2\text{O}_4\cdot 2\text{CH}_2\text{O}\cdot 4\text{H}_2\text{O}$ (compare H. Schmid, *Bull. Soc. Ind. Mulhouse*, 1904, 74, 63), which can be separated by fractional crystallisation from dilute alcohol into equal parts of formaldehyde sodium hydrogen sulphite and formaldehyde sodium hydrogen hyposulphite, $\text{NaHSO}_2\cdot\text{CH}_2\text{O}\cdot 2\text{H}_2\text{O}$ (Zundel, *ibid.*, 49). The latter crystallises from water in large, transparent, monoclinic (?) prisms, melts at 63—64°, begins to lose water of crystallisation at 120°, at 125° evolves formaldehyde and hydrogen sulphide, and finally leaves a residue of sodium sulphide. Mineral acids decompose it with the formation of sulphur and hydrogen sulphide ; alkalis regenerate sodium hyposulphite and formaldehyde, and sodium hydroxide followed by ammonia solution furnishes disodium hyposulphite and hexamethylenetetra-amine. The *lead* derivative is insoluble in water, but dissolves in dilute nitric or in acetic acid to form a strongly reducing solution. The compound can be applied as a reducing agent when warmed in presence of alkalis or sodium hydrogen sulphite and, in these circumstances, gives good results in the conversion of nitro-derivatives into the corresponding amines.

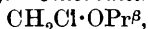
The authors consider that these observations confirm the validity of

the formula H_2SO_2 assigned by Schutzenberger to hyposulphurous acid (*Compt. rend.*, 1869, 69, 196). T. A. H.

Constitution of Aldehydesulphurous Acid and Hypo-sulphurous Acid. KARL REINKING, ERICH DEHNEL, and HANS LABHARDT (*Ber.*, 1905, 38, 1069—1080. Compare preceding abstract and this vol., ii, 240).—Hydroxymethanesulphonic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ (compare Müller, this Journal, 1874, 45), is best prepared by cautiously adding 50 per cent. sulphur trioxide to a cooled mixture of methyl alcohol and sulphuric acid monohydrate. The *sodium* salt crystallises in needles grouped in stellar aggregates and can be heated with acids and alkalis without change.

Aminomethyl hydrogen sulphite, $\text{NH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_2\text{H}$, prepared by the interaction of formaldehyde, sodium hydrogen sulphite, and ammonia, forms colourless crystals decomposing at 193° ; on reduction with zinc dust and acetic acid, *zinc aminomethylsulphoxylate* is formed. Both sodium hyposulphiteformaldehyde and formaldehydesulphoxylate form compounds with amines; *sodium o-toluidinoformaldehydesulphoxylate*, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}\cdot 3\text{H}_2\text{O}$, has been analysed. It is clearly proved that hydroxymethanesulphonic acid and formaldehyde sulphurous acid are not identical. E. F. A.

Chloro-derivatives of Propyl and isoPropyl Formals. LÉON STAPPERS (*Bull. Acad. roy. Belg.*, 1904, 1161—1170. Compare Henry, Abstr., 1904, i, 364).—*Chloromethyl isopropyl ether*,



obtained by the action of hydrogen chloride on formaldehyde in presence of isopropyl alcohol, is a colourless, mobile liquid with a pungent odour; it boils at $101\text{--}102^\circ$ under 760 mm. pressure, has a sp. gr. 0.972 at 20° and n_D 1.41136 at 18° . It evolves hydrogen chloride on exposure to moist air.

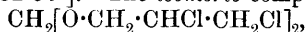
Chloromethyl a-chloroisopropyl ether, $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl}$, similarly prepared, is a colourless liquid which boils at $162\text{--}164^\circ$ under 763 mm. pressure and has a sp. gr. 1.197 at 20° .

The isopropyl formals and their derivatives may be obtained by the action of hydrogen chloride on formaldehyde in presence of 2 mols. of the appropriate isopropyl compound, or by the interaction of the latter with trioxymethylene in presence of ferric chloride (compare Arnhold, Abstr., 1887, 912).

s-aa-Dichloroisopropyl formal, $\text{CH}_2[\text{O}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl}]_2$, is a colourless, mobile liquid with a sharp, bitter taste; it boils at $227\text{--}228^\circ$ under 758 mm. pressure, has a sp. gr. 1.150 at 20° and n_D 1.45607 at 20° . The isomeric *s-ββ-dichloropropyl formal*, $\text{CH}_2[\text{O}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_3]_2$, prepared from propylene β-chlorohydrin (Henry, Abstr., 1903, i, 725), boils at 228° , has a sp. gr. 1.145 at 20° and n_D 1.45307.

s-Tetrachloroisopropyl formal, $\text{CH}_2[\text{O}\cdot\text{CH}(\text{CH}_2\text{Cl})_2]_2$, obtained by the action of trioxymethylene on *s*-glyceryl dichlorohydrin in presence of ferric chloride, melts at 51° , boils at 220° under 107 mm. pressure, is soluble in benzene or chloroform, and slightly so in light petroleum. It forms crystals belonging to the monoclinic system [$a:b:c=$

2.787 : 1 : 1.384 ; $\alpha = 82^\circ 50'$. The *isomeric* compound,



similarly obtained from *as*-glyceryl dichlorohydrin, is a colourless, viscid liquid having sp. gr. 1.370 and n_D 1.49399 at 20° . T. A. H.

Condensation of Methyleneethylacraldehyde with *iso*Butaldehyde. WILHELM MORAWETZ (*Monatsh.*, 1905, **26**, 127—132).—The *aldol*, $\text{CHEt} \cdot \text{CMe} \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{COH}$, formed by the condensation of methyleneethylacraldehyde with *isobutaldehyde* in alcoholic potassium hydroxide solution, is a viscid, yellow oil, which boils at 130 — 140° under 11 mm. pressure, reduces ammoniacal silver solutions, and forms an *additive* compound with 1 mol. of bromine in chloroform solution. The *oxime*, $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N}$, is a viscid, yellow oil, which boils at 160 — 170° under 18 mm. pressure; the *acetyl* derivative, $\text{C}_{12}\text{H}_{20}\text{O}_3$, is an oil which decomposes on distillation. When boiled with silver oxide and water, the aldol yields the *silver* salt of the corresponding hydroxy-acid, $\text{C}_{10}\text{H}_{17}\text{O}_3\text{Ag}$, which crystallises in glistening leaflets on concentration of the aqueous solution over sulphuric acid in a vacuum.

G. Y.

The Diphenylhydrazones of *l*-Arabinose and of Xylose. BERNHARD TOLLENS and A. D. MAURENBRECHER (*Ber.*, 1905, **38**, 500—501. Compare Neuberg, *Ber.*, 1904, **37**, 4618).—Müther and Tollens' statement (*Abstr.*, 1904, i, 224) that *l*-arabinosediphenylhydrazone melts at 204 — 205° is confirmed. This hydrazone has also been obtained by the action of diphenylhydrazine on the products formed during the hydrolysis of cocoa beans.

J. J. S.

***iso*Maltose.** EDUARD JALOWETZ (*Zeit. angew. Chem.*, 1905, **18**, 171).—The crystalline form and the appearance of maltosazone vary according to the mode of preparation (compare Ost, this vol., i, 22).

A. McK.

Reversion of Amylocellulose into Starch. EUGÈNE ROUX (*Compt. rend.*, 1905, **140**, 440—442).—Maquenne has shown that starch paste slowly reverts into amylocellulose (compare *Abstr.*, 1903, i, 679; 1904, i, 17, 227, 228, 294, 800). In the present paper, the reaction is shown to be a reversible one between the temperatures of 0° and 150° ; at the higher temperature, and in the presence of excess of water, the amylocellulose liquefies after 10 minutes, and on cooling forms a starch paste or jelly which is coloured blue by iodine; if, however, the heating is prolonged to about 3 hours, the solution on cooling deposits spherical granules of artificial starch, closely resembling the natural grains in their appearance under the microscope, and like them being coloured blue by iodine; they do not, however, form a jelly with boiling water. If the amylocellulose is heated with water at 150° for a longer period than 3 hours, amyloextrin is formed, which gives a yellow colour with iodine and breaks down on continued heating into dextrans and dextrose. Amylocellulose, natural and artificial starch are to be regarded as different condensa-

tion forms of the same fundamental chemical nucleus (compare Maquenne, Abstr., 1904, i, 294). M. A. W.

Optically Active Nitrogen Compounds. Miss M. R. THOMAS and HUMPHREY O. JONES (*Proc. Camb. Phil. Soc.*, 1905, 13, 33—34. Compare *Trans.*, 1904, 85, 223; 1905, 87, 135).—*Phenylbenzylmethylisopropylammonium iodide*, prepared by mixing methylisopropylaniline with benzyl iodide in molecular proportions, melts at 133°. When this is treated with the calculated quantity of silver *d*-bromocamphorsulphonate in ethyl acetate solution and the product crystallised three times from ethyl acetate or water, *l*-phenylbenzylmethylisopropylammonium *d*-bromocamphorsulphonate is obtained. In dilute aqueous solution, $[M]_D - 123^\circ$. Subtracting the rotation due to the acid ion, the value of $[M]_D$ for the basic ion is obtained, -393° .

l-Phenylbenzylmethylisopropylammonium iodide is obtained by precipitating the aqueous solution of the bromocamphorsulphonate by a solution of potassium iodide. It melts at 132° and crystallises in the tetragonal system, whereas the crystals of the inactive iodide belong to the oblique system, from which it is concluded that the latter must be a racemic compound. The active iodide is stable in alcoholic solution; it racemises quickly in chloroform solution. In absolute alcohol, $[M]_D - 428^\circ$.

i-Phenylbenzylmethylisoamylammonium iodide forms small prisms melting at 156°. On preparing the *d*-camphorsulphonate and crystallising from acetone, the salt of the *l*-base was obtained after twenty crystallisations, although not perfectly pure. It melts at 178—178.5°; in dilute aqueous solution, $[M]_D - 317^\circ$, from which, for the basic ion, $[M]_D - 370^\circ$ is calculated. The corresponding active iodide melts at 156°; in ethyl alcohol, $[M]_D - 478^\circ$. It racemises in chloroform solution.

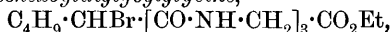
Substitution of *isopropyl* or *isoamyl* for the ethyl group in the phenylbenzylmethylethylammonium ion thus causes a change in the molecular rotation of more than 350° and 370° respectively. Substitution of these for the allyl group also increases the molecular rotation to a great extent, since for the phenylbenzylmethylallylammonium ion $[M]_D = 166^\circ$. H. M. D.

Copper and Nickel Salts of some Amino-acids. GIUSEPPE BRUNI (*Zeit. Elektrochem.*, 1905, 11, 93—94).—A claim for priority (see Bruni and Fornara, Abstr., 1904, i, 855, and H. Ley, this vol., i, 175). T. E.

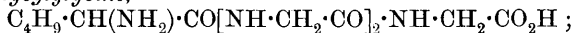
Synthesis of Polypeptides. IX. Chlorides of the Amino-acids and their Acyl Derivatives. EMIL FISCHER [with F. REUTER] (*Ber.*, 1905, 38, 605—619. Compare Abstr., 1903, i, 465, 607, 799; 1904, i, 652, 771, 867, 890; this vol., i, 30, 31).—Two new reactions are described, namely, the preparation of amino-acid chlorides by the interaction of the acids with phosphorus pentachloride and acetyl chloride, and the splitting of the ring in diketopiperazine derivatives by means of dilute alkalis, which very much facilitate the synthesis of derivatives of polypeptides.

Thus, on shaking glycine anhydride with the equivalent quantity of normal sodium hydroxide, it is converted into the alkali salt of glycylglycine, and this, on further treatment with acid chlorides, such as benzoyl chloride, yields benzoylglycylglycine. Alanine anhydride acts in a similar manner, but leucinimide is only hydrolysed with great difficulty.

Ethyl α -bromoisohexoyldiglycylglycine,



can be prepared either by the action of acetyl chloride and phosphorus pentachloride on α -bromoisohexoylglycylglycine and subsequent combination of the chloride formed with ethyl glycine, or, still better, by the interaction of ethyl glycylglycine with the chloride of α -bromoisohexoylglycine. It melts at 184.5° (corr.) and crystallises in stellar aggregates or clusters of colourless needles. The corresponding α -bromoisohexoyldiglycylglycine melts at 168° (corr.), crystallises from alcohol in minute needles, and is converted by dilute ammonia into leucyldiglycylglycine,



this darkens at 215° , melts to a dark liquid at 233° (corr.), and gives the biuret reaction.

Hippuryl chloride, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COCl}$, is easily prepared by the action of acetyl chloride and phosphorus pentachloride on hippuric acid; it crystallises from acetyl chloride in colourless needles, becomes yellow at 125° and then dark red, and melts at a higher temperature. Alcohol or water converts the chloride into hippuric acid; with ethereal ammonia, hippuramide, melting at 183° , is formed. Hippuryl chloride reacts readily with ethyl glycine, either in ethereal or alkaline solution, forming the benzoylglycylglycine melting at 206° , described by Curtius and Wüstenfeld (Abstr., 1904, i, 833).

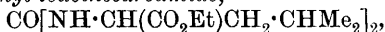
Leucyl chloride hydrochloride, $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NH}_3\text{Cl})\cdot\text{COCl}$, is prepared by the combined action of acetyl chloride and phosphorus pentachloride on leucine, special precautions being taken to exclude all traces of moisture, while the product is filtered and washed. The salt is relatively stable towards heat, but is decomposed at once by water into leucine and hydrogen chloride; it reacts with ethyl glycine in ethereal solution, forming *ethyl leucylglycine*, which was isolated as *leucylglycine anhydride*, $\text{C}_4\text{H}_9\cdot\text{CH}\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\end{smallmatrix}\rangle\text{CH}_2$, crystallising in colourless needles and melting at 244° .

Alanyl chloride hydrochloride, $\text{NH}_3\text{Cl}\cdot\text{CHMe}\cdot\text{COCl}$, prepared as above, forms a colourless, crystalline mass which sinters about 110° . *α -Aminobutyryl chloride hydrochloride*, $\text{CH}_2\text{Me}\cdot\text{CH}(\text{NH}_3\text{Cl})\cdot\text{COCl}$, forms well-defined crystals.

E. F. A.

The Carbimide of Natural (*l*) Leucine. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1905, 140, 505—506. Compare this vol., i, 178).—Natural (*l*) leucine reacts with carbonyl chloride in toluene solution at 130° to form leucinecarbimide (compare Vittenet, Abstr., 1899, i, 756; 1900, i, 153), which, however, could not be isolated in a pure state; the *ethyl ester*, $\text{CO}\cdot\text{N}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CHMe}_2$, obtained

together with *diethyl leucinecarbamide*,



boiling at 180—190° under 18 mm. pressure, by the action of carbonyl chloride in toluene solution at 130° on the ethyl ester of leucine (compare Fischer, Abstr., 1901, i, 192), is a colourless liquid boiling at 120—130° under 18 mm. pressure, having a disagreeable odour, and emitting irritating vapours; it reacts with alcohols to form urethanes, is insoluble in water, and soluble in benzene, ether, or chloroform. M. A. W.

Mercury Thiocyanate Complexes. MILES S. SHERRILL and S. SKOWRONSKI (*J. Amer. Chem. Soc.*, 1905, 27, 30—47).—Sherrill (Abstr., 1903, ii, 534) has investigated the mutual relations of mercuric chloride, bromide, iodide, and cyanide to the corresponding potassium salts with special reference to the formation of complexes. This work has now been extended to mercuric thiocyanate.

The results of solubility, freezing point, and *E.M.F.* determinations have shown that in aqueous solution a complex salt, $\text{K}_2\text{Hg}(\text{SCN})_4$, is formed. The same salt is produced when mercurous thiocyanate is treated with potassium thiocyanate, mercury being liberated.

A comparison of the stability constants of the mercuric complexes shows that the relative tendency of the halogens and of cyanogen and thiocyanogen groups to form complexes increases in the order Cl, Br, SCN, I, CN, a result which agrees with the observations of Grossmann (Abstr., 1904, i, 147) and Bodländer and Eberlein (Abstr., 1904, ii, 401).

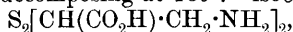
The solubility product of mercurous thiocyanate, $[\text{Hg}^{++}][\text{SCN}^-]^2$, has been deduced from the results of experiments described in this paper and found to be 1.8×10^{-20} . E. G.

Aminoacetone. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 752—753. Compare Abstr., 1893, i, 734; 1903, i, 13; Alexander, this vol., i, 92).—The action of hydrogen cyanide on aminoacetone hydrochloride at the ordinary temperature leads to the formation of a *substance*, $(\text{C}_4\text{H}_6\text{N}_2)_n$, which is obtained in crystalline nodules or thin rhomboids, sinters at 180°, melts and decomposes at 190—192°, volatilises without melting when slowly heated, and when boiled with water undergoes decomposition into its generators. G. Y.

isoCysteine and isoCystine. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 630—646).— γ -Hydroxypropylphthalimide, melting at 75° (compare Abstr., 1890, 472), is converted, on oxidation with potassium dichromate, into *phthalyl- β -alanine*, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, melting at 150—151°; the *ethyl* ester separates in flat needles melting at 73.5°. The corresponding *phthalyl- α -alanine*, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, forms colourless needles melting at 160—162° and an *ethyl* ester melting at 61—63° (compare Andreasch, Abstr., 1904, i, 895). It was found impossible to brominate either of the phthalylalanines.

Dihydrouracil, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{NH} \\ \text{CO}-\text{NH} \end{smallmatrix}\rangle\text{CO}$, may be prepared either by the

interaction of β -alanine hydrochloride, obtained from the phthalyl derivative, dissolved in normal potassium hydroxide, with potassium isocyanate or directly from β -iodopropionic acid, the latter method being the more convenient. By bromination at 100° in glacial acetic acid in a special apparatus, the bromodihydrouracil described by Fischer and Roeder (Abstr., 1901, i, 294) was obtained, crystallising in flat needles or plates, melting at 195° , and decomposing into uracil and hydrogen bromide at a slightly higher temperature. *Thiocyanodihydrouracil*, obtained from this by the action of potassium thiocyanate in alcohol, crystallises in needles melting at $202\text{--}203^\circ$ to a brown liquid. By the action of fuming hydrochloric acid at 170° , it is converted into *isocysteine hydrochloride*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{SH})\cdot\text{CO}_2\text{H}\cdot\text{HCl}$, melting and decomposing at 141° , which gives a brownish-black precipitate with copper sulphate, dissolving in excess to a characteristic purple solution. Iodine converts it into *isocystine hydriodide*, $\text{S}_2[\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{NH}_2]_2\cdot\text{HI}$, which separates from water in glistening crystals melting and decomposing at 189° . *isoCystine*,



sinters at 180° and melts to a reddish-brown mass at 185° ; it gives a black coloration with cold alkaline lead solutions and a blackish-brown coloration with copper sulphate.

isoCysteine hydrochloride is oxidised by bromine water to *isocysteinic acid*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{CO}_2\text{H}$, crystallising in well-defined octahedra and pyramids which melt and decompose at $272\text{--}274^\circ$; it forms a well-defined blue copper salt.

Anilnodihydrouracil, $\text{NHPh}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{NH} \\ \text{CO}\text{--}\text{NH}\end{smallmatrix}\right\rangle\text{CO}$, formed by the interaction of bromodihydrouracil and aniline, crystallises in colourless, quadratic plates which sinter at 229° and melt and decompose at 239° . On heating it with hydrochloric acid at 170° , phenylethylenediamine, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPh}$, is formed, melting at $199\text{--}200^\circ$ and yielding a picrate melting at $179\text{--}180^\circ$ (Abstr., 1889, 1166).

The formation of this diamine confirms the assumed formula of bromodihydrouracil. E. F. A.

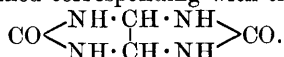
Solubility and Heat of Solution of Carbamide. Energy Equilibrium. OTTO KRUMMACHER (*Zeit. biol.*, 1905, 28, 302—321. Compare Rubner, *ibid.*, 20, 414).—The specific heat of a 1.804 per cent. aqueous carbamide solution is 0.988; the heat of combustion of pure carbamide is 2.532 Cal. and the heat of solution 3.57 Cal. The numbers varied somewhat according to the calorimeter employed. With a small calorimeter, the mean value was 3.54, and with a large calorimeter 3.62. All possible precautions were taken. Previous determinations are: Rubner, 3.679; Berthelot and Petit, 3.580; J. Thomsen, 3.349; and Speyers, 3.628.

The solubility of carbamide in water at different temperatures has been determined. One gram of water dissolves 0.779 gram of carbamide at 5.5° , 1.000 at 17.1° , and 1.094 at 20.92° . The heat of solution has been calculated from the data to be 3.608 Cal. for 5.5° and 20.9° .

J. J. S.

Oxaluramide. MARTIN SCHENCK (*Ber.*, 1905, **38**, 459—461).—In the preparation of oxaluramide (Rosing and Schischkoff, *Annalen*, 1858, **106**, 255; Strecker, *ibid.*, 1860, **113**, 47) it is essential that a large excess of ammonia should not be employed, as concentrated ammonium hydroxide converts the amide into carbamide and ammonium oxalate and oxamate. Oxaluramide is not readily decomposed by hot water, and when subjected to destructive distillation yields ammonia, water, cyanic acid, and probably cyanuric acid and biuret. J. J. S.

Attempted Synthesis of Uric Acid. HENRY J. H. FENTON (*Proc. Camb. Phil. Soc.*, 1905, **13**, 25—26).—Trihydroxyacrylic acid, the parent acid, which on condensation with carbamide would be expected to yield uric acid, is as yet unknown. On oxidation of dihydroxymaleic acid with ferric or mercuric salts, the semialdehyde of mesoxalic acid, $\text{CHO} \cdot \text{CO} \cdot \text{CO}_2\text{H}$, is obtained. On the assumption that the aldehyde hydrate of this might be tautomeric with trihydroxyacrylic acid, the author has condensed the semialdehyde with carbamide. When the condensation is carried out in aqueous solution, carbon dioxide is evolved and glycoluril is obtained corresponding with the formula



This is probably produced by the decomposition of glycolurilcarboxylic acid.

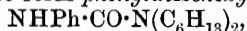
When glycoluril is evaporated to dryness on a water-bath with concentrated nitric acid and the residue treated with sodium hydroxide, a slight pink or orange colour is developed which, on addition of sodium hypochlorite, changes to an intense purple. H. M. D.

[Acetyl-lactonitrile. Acetylsalicylphenetidide.] Correction. RICHARD ANSCHÜTZ (*Ber.*, 1905, **38**, 719).—Acetyl-lactonitrile (*Abstr.*, 1904, i, 966) and acetylsalicylphenetidide (*ibid.*, 990), which were described as new substances, had been prepared previously.

W. A. D.

Application to Nitriles of the Method of Direct Hydrogenation by Catalysis; Synthesis of Primary, Secondary, and Tertiary Amines. PAUL SABATIER and JEAN B. SENDERENS (*Compt. rend.*, 1905, **140**, 482—486).—Aliphatic nitriles are directly hydrogenated in the presence of reduced nickel at 180° to 220° to the corresponding primary amine according to the equation $\text{C}_n\text{H}_{2n+1}\cdot\text{CN} + 2\text{H}_2 = \text{C}_n\text{H}_{2n+1}\text{CH}_2\cdot\text{NH}_2$, which at the high temperature employed is partially converted into the corresponding secondary and tertiary amines and ammonia according to the equations $2\text{NH}_2\cdot\text{CH}_2\cdot\text{C}_n\text{H}_{2n+1} = \text{NH}_3 + \text{NH}(\text{CH}_2\cdot\text{C}_n\text{H}_{2n+1})_2$; $3\text{NH}_2\cdot\text{CH}_2\cdot\text{C}_n\text{H}_{2n+1} = 2\text{NH}_3 + \text{N}(\text{CH}_2\cdot\text{C}_n\text{H}_{2n+1})_3$ (compare *Abstr.*, 1904, i, 305, 661); the final product, therefore, is a mixture of the three amines in which the secondary amine preponderates when the reaction is conducted at about 200° ; thus, in the case of acetonitrile, diethylamine constituted 3/5ths of the mixed amines, whilst propionitrile yielded on reduction 1 part of propylamine, 8 to 9 parts of dipropylamine, and 2 parts of

tripropylamine. Hexonitrile (α -cyano- γ -methylbutane), on direct hydrogenation at $200-220^\circ$, yields (1) 5 parts of β -methylpentane boiling at 62° , formed by the complete reduction of the nitrile; (2) 8 parts of α -amino- δ -methylpentane, $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$, a colourless liquid with a disagreeable odour, boiling at 125° under 762 mm. pressure, slightly soluble in water, turning blue litmus red, forming a soluble *hydrochloride*, and uniting directly with carbon dioxide to form a *carbonate* crystallising in small, white prisms; the *oxalate* crystallises in long, thin needles melting at 166° , slightly soluble in water, readily so in warm alcohol, and it reacts with phenylcarbimide to form *phenylisohexylcarbamide*, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_{13}$, which crystallises from alcohol in thin, white needles melting at 84° ; (3) *diisohexylamine*, $\text{NH}(\text{C}_3\text{H}_7 \cdot \text{CHMe}_2)_2$, a colourless liquid with a disagreeable odour, boiling at 134° under 35 mm. pressure or 225° under 762 mm., having a sp. gr. 0.797 at $0^\circ/0^\circ$, is strongly alkaline towards litmus, and forms an unstable crystalline *carbonate*, an *oxalate* crystallising from alcohol in pearly plates which decompose at 220° , and combines with phenylcarbimide to form *phenyldiisohexylcarbamide*,



which crystallises from alcohol in voluminous, colourless prisms melting at 104° ; (4) *triisohexylamine*, $\text{N}(\text{C}_3\text{H}_7 \cdot \text{CHMe}_2)_3$, a yellow liquid with a disagreeable odour boiling at 178° under 35 mm. or at 283° under 762 mm. pressure, has a sp. gr. 0.807 at $0^\circ/0^\circ$, and forms a crystalline *oxalate* melting and decomposing above 250° .

The aromatic nitriles are converted almost exclusively into the corresponding hydrocarbon and ammonia on direct hydrogenation in the presence of nickel at 200° ; thus benzonitrile yielded toluene and ammonia.

M. A. W

Trimercuriacetaldehyde. KARL A. HOFMANN (*Ber.*, 1905, 38, 663. Compare Biltz, this vol., i, 165).—A claim for priority in reference to the aldehydic nature of the precipitate caused by acetylene in mercury chloride solutions (see also Abstr., 1899, i, 97).

E. F. A.

Preparation of cycloHexene from cycloHexanol. LÉON BRUNEL (*Bull. Soc. chim.*, 1905, [iii], 33, 270—271. Compare Abstr., 1903, i, 680, 695, and Zelinsky and Zelikoff, Abstr., 1902, i, 2).—When cyclohexanol is treated with phosphoric oxide, zinc chloride, or potassium hydrogen sulphate, cyclohexene is formed; the yield with zinc chloride varies from 65 to 70 per cent. and with potassium hydrogen sulphate from 82—83 per cent. of the theoretical, the loss in each case being due to the formation of condensation products. A description of the best method of carrying out the operation is given. T. A. H.

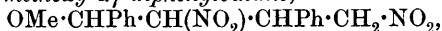
The Friedel and Crafts Reaction. JACOB BOESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 470—473. Compare Abstr., 1903, i, 617; 1904, i, 384).—A discussion of the mechanism of the Friedel-Crafts reaction.

A. McK.

Action of Alkalis on Phenylnitroethylene. JAKOB MEISENHEIMER and FRIEDRICH HEIM (*Ber.*, 1905, 38, 466—473).—An ice-cold suspension of phenylnitroethylene in aqueous methyl alcohol readily reacts with a solution of sodium methoxide, yielding a clear solution containing presumably the compound $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{NO}\cdot\text{ONa}$, from which β -nitro- α -methoxy- α -phenylethane, $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}_2$, can be obtained by means of carbon dioxide. It is a colourless oil and distils at 135—136° under 12 mm. pressure. It is not decomposed when the ethereal solution is boiled with concentrated hydrochloric acid, and the addition of mineral acids to solutions of its alkali salts yields phenylnitroethylene. β -Nitro- α -ethoxy- α -phenylethane distils at 136—137° under 12 mm. pressure.

β -Nitro- α -hydroxy- α -phenylethane cannot be obtained in a pure state by the action of carbon dioxide on an aqueous solution of its sodium derivative (Thiele and Haackel, *Abstr.*, 1903, i, 160).

$\beta\delta$ -Dinitro- α -methoxy- α -diphenylbutane,



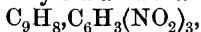
is formed when the alkaline solution, obtained in the preparation of nitromethoxyphenylethane, is kept for some 40 hours, and a current of carbon dioxide then passed through without the addition of water. The yield varies from 15—35 per cent. The product crystallises from methyl alcohol in large, colourless needles, melts at 151—152°, is only sparingly soluble in ether or cold methyl or ethyl alcohol, and does not readily reduce alkaline permanganate. Its alkaline solution reacts with benzenediazonium acetate solution (Bamberger, *Abstr.*, 1899, i, 108), yielding a *monophenylhydrazone*, $\text{C}_{23}\text{H}_{22}\text{O}_5\text{N}_4$, melting and decomposing at 169—170°; the same compound is obtained even in the presence of excess of the diazonium solution. Bromine water reacts with an alkaline solution yielding a *tribromo-derivative*, $\text{C}_{17}\text{H}_{15}\text{O}_5\text{N}_2\text{Br}_3$, melting and decomposing at 182°.

Sodium and potassium salts have been obtained, for example, $\text{C}_{17}\text{H}_{16}\text{O}_5\text{N}_2\text{Na}_2\cdot 2\text{MeOH}$, but they are very unstable.

$\beta\delta$ -Dinitro- α -ethoxy- α -diphenylbutane crystallises in felted needles and melts at 156°.

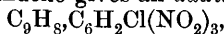
J. J. S.

Picrates and other Additive Products of Unsaturated Compounds. GIUSEPPE BRUNI and ERCOLE TORNANI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 154—157. Compare *Abstr.*, 1904, i, 875).—Indene and *s*-trinitrobenzene yield an *additive compound*,



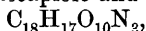
which separates from ethereal solution in long, lemon-yellow needles melting at 101—102°.

With picryl chloride, indene gives an *additive compound*,



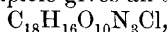
which crystallises from ether in long, lemon-yellow needles melting at 39°.

The *additive compound* of *isopiole* and *s*-trinitrobenzene,



is deposited from alcohol in dark orange, silky, acicular crystals melting at 66—67°.

With picryl chloride, *iso*apiole gives an *additive compound*,

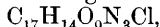


which separates from alcohol in rose-red, acicular crystals melting at 55—56°.

*iso*Apiole from dill oil and *s*-trinitrobenzene yield an *additive compound*, $\text{C}_{18}\text{H}_{17}\text{O}_{10}\text{N}_3$, which crystallises from alcohol in shining, red needles melting at 76—77°.

Picryl chloride and *iso*apiole from dill oil form an *additive compound*, $\text{C}_{18}\text{H}_{16}\text{O}_{10}\text{N}_3\text{Cl}$, which separates from alcohol in red, acicular crystals melting at 43—44°.

*iso*Myristicin and picryl chloride give an *additive compound*,



which crystallises from alcohol in dark red prisms melting at 65—66°.

Tolane picrate, $\text{C}_{14}\text{H}_{10}, 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from ether in pale yellow plates which melt at 111° and explode at a higher temperature.

Quinone picrate, $\text{C}_6\text{H}_4\text{O}_2, \text{C}_6\text{H}_7\text{O}_7\text{N}_3$, separates from ether in large, lemon-yellow crystals melting at 78—79°.

T. H. P.

Melting Point Curve for Mixtures of Anthracene and Picric Acid. ROBERT KREMANN (*Monatsh.*, 1905, **26**, 143—148. Compare this vol., ii, 76, 77).—The melting point curve for mixtures of anthracene and picric acid falls from the melting point of anthracene to about 141°, where there is a break, and then to a eutectic point at about 106° for a mixture containing about 86 molecular per cent. of picric acid; the break at 141° represents the eutectic point between the molecular additive compound which melts at 152·5° (Behrend, *Abstr.*, 1895, ii, 71) and anthracene.

G. Y.

Syntheses in the Anthracene Series. IV. Tetra-alkyl Derivatives of 9:10-Diaminodiphenyl-9:10-diphenyldihydroanthracene. ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1905, **140**, 343—345. Compare *Abstr.*, 1904, i, 314, 660, and this vol., i, 188).—9:10-Dihydroxy-9:10-diphenyldihydroanthracene readily condenses with dimethyl- or diethyl-aniline in acetic acid solution, and the product consists of equal quantities (45 per cent. of each) of the *cis*- and *trans*-stereoisomerides of the corresponding 9:10-tetra-alkyldiaminodiphenyl-9:10-diphenyldihydroanthracenes, which are readily separated by their difference in solubility and melting point. The first form, 9:10-tetramethyldiaminodiphenyl-9:10-diphenyldihydroanthracene, $\text{C}_{14}\text{H}_5\text{Ph}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, forms small, brilliant prisms melting above 360° and almost insoluble in the ordinary solvents; the *platinichloride* forms thin, yellow needles; the second form is obtained in white crystals melting at 275°, more readily soluble than its isomeride; the *platinichloride* is slowly deposited from solution in golden leaflets. The two stereoisomerides of 9:10-tetraethyldiaminodiphenyl-9:10-diphenyldihydroanthracene are colourless, crystalline compounds melting at 250° and 230° respectively.

M. A. W.

Structural Formula for Triphenylmethyl. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1905, **38**, 771—773. Compare this vol., i, 125, and Jacobson, *ibid.*, 186).—Further arguments in favour of the

hexaphenylethane formula for Gomberg's triphenylmethyl are brought forward, but the question is not regarded as finally settled.

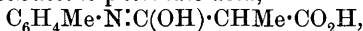
J. J. S.

Action of Ethyl *iso*Succinate on Aniline, *p*-Toluidine, and *p*-Aminophenol. EZIO COMANNUCCI and R. LOBELLO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iiia], 11, 18—27).—The interaction of molecular proportions of aniline and ethyl *iso*succinate at 180° yields: (1) *isosuccinodianilide*, $\text{CHMe}(\text{CO}\cdot\text{NHPh})_2$, which crystallises from alcohol in shining, white, silky scales melting at 214° and dissolves in acetic acid and, to a slight extent, in chloroform or benzene; with concentrated nitric acid, it gives first a brown and then a green coloration, but with ferric chloride its alcoholic solution yields no coloration. (2) *Ethyl isosuccinanilate*, $\text{NPh}\cdot\text{C}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, which separates from the mother liquor in microscopic, white crystals melting at 173—174° and soluble in the same solvents as the above compounds; with fuming nitric acid, it gives oily, reddish-brown drops, whilst with ferric chloride the alcoholic solution yields a brownish-red solution which changes to violet and later to grey on dilution with water. *isoSuccinanilic acid*, $\text{NPh}\cdot\text{C}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, forms a white, crystalline powder which begins to melt and decompose at 175° and melts into a red liquid at 180°.

The interaction of molecular proportions of *p*-toluidine and ethyl *iso*succinate at 180° yields: (1) *isosuccinodi-p-toluidide*,



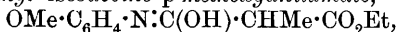
which crystallises from alcohol in slender, silky needles melting at 245° and dissolves in acetic acid and, to a slight extent, in chloroform or benzene; with fuming nitric acid, it gives an orange solution which deposits yellow flocks on the addition of water; its alcoholic solution gives no coloration with ferric chloride. (2) *Ethyl isosuccino-p-toluidate*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{C}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$, which crystallises from alcohol in large, transparent plates melting at 85—87° and dissolving in acetic acid, chloroform, or benzene; it is turned yellow by fuming nitric acid, and its alcoholic solution gives an intense reddish-violet coloration with ferric chloride. *isoSuccino-p-toluidic acid*,



separates in white needles, which melt and decompose at 145° and in alcoholic solution yields a pale red coloration with ferric chloride.

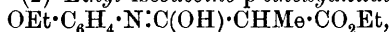
isoSuccinodi-p-hydroxyanilide, $\text{CHMe}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$, obtained from *p*-aminophenol and ethyl *iso*succinate, separates from benzene in dirty-white crystals melting at 136—137° and gives a yellow coloration with fuming nitric acid, but none with ferric chloride.

The interaction of molecular proportions of *p*-anisidine and ethyl *iso*succinate at 170—175° yields: (1) *isosuccinodi-p-methoxyanilide*, $\text{CHMe}(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, which crystallises from alcohol in white needles melting at 200—201° and is soluble in acetic acid and, to a slight extent, in benzene or chloroform; with fuming nitric acid, it gives an orange liquid yielding a yellow, flocculent precipitate with water, whilst its alcoholic solution gives a faint green coloration with ferric chloride. (2) *Ethyl isosuccino-p-methoxyanilamate*,



which separates from alcohol in white crystals melting at 112—114° and behaves towards fuming nitric acid, ferric chloride, and organic solvents like the previous compound. *isoSuccino-p-methoxyanilic acid*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, is a white, crystalline compound melting and decomposing at 143° and is soluble in water or acetic acid, and slightly so in benzene or chloroform; in alcoholic solution, it gives a reddish-yellow coloration with ferric chloride.

The interaction of *p*-phenetidine and ethyl *isosuccinate* in molecular proportions at 190—192° yields: (1) *isosuccinodi-p-ethoxyanilide*, $\text{CHMe}(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$, which crystallises from alcohol in shining, white needles melting at 210° and resembles the preceding diamides in its behaviour towards concentrated nitric acid, ferric chloride, and organic solvents. (2) *Ethyl isosuccino-p-ethoxyanilate*,



which forms small, white needles melting at 125—126° to a violet liquid; in alcoholic solution, it gives a violet coloration; with ferric chloride and with concentrated nitric acid, it yields an orange solution from which water precipitates a yellow, flocculent nitro-derivative. *isoSuccino-p-ethoxyanilic acid*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, forms silky, white crystals which melt at 146—148° and dissolve in alcohol or acetic acid and, to a slight extent, in benzene or chloroform; with ferric chloride, it gives a pale orange coloration. T. H. P.

Preparation of Pure *o*-Toluidine and a Method for Ascertaining its Purity. ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 395).—In order to estimate the amount of *p*-toluidine in admixture with *o*-toluidine, the solidifying point of the acetylated product was determined. The following figures for the solidifying point of a mixture of aceto-*o*- and *p*-toluidides were obtained: 109·15°, 108·45°, 107·75°, 103·2°, and 100·8°, corresponding with 0, 1·12, 2·42, 9·58, and 13·6 per cent. of the para-compound.

Details are quoted to show how small amounts of *p*-toluidine and of aniline may be detected by means of the solidifying point figures, the *o*-toluidine being mixed in one case with 2 per cent. of aniline and in another with 2 per cent. of *p*-toluidine. A. McK.

Benzylmalimides. ALBERT LADENBURG and WALTER HERZ (*J. pr. Chem.*, 1905, [ii], 71, 152).—A reply to Lutz (this vol., i, 191).

G. Y.

Amide Formation between Optically Active Acids and Bases. The Optically Active α -Aminoethylbenzenes. WILLY MARCKWALD and R. METH (*Ber.*, 1905, 38, 801—810).—The method of Marckwald and McKenzie (*Abstr.*, 1899, ii, 733; 1900, i, 207; 1901, ii, 229) for resolving inactive substances into their optically active components has been applied by the authors to the resolution of an inactive acid by an active base and of an inactive base by an active acid.

When equal weights of *r*-mandelic acid and *l*-menthylamine are

heated together for 10 hours at 160—170°, the product is a mixture of menthylamine mandelate and mandelmenthylamide, which, when agitated with aqueous sodium hydroxide, yields sodium mandelate; from this, a levorotatory mandelic acid, having $[\alpha]_D - 5.1^\circ$ ($c = 12.5$) in aqueous solution, was prepared. *d*-Mandelic acid is accordingly more quickly converted into amide by *l*-methylamine than is *l*-mandelic acid. The ratio of the rate of amide formation between *l*- and *d*-mandelic acids respectively and *l*-menthylamine, calculated by the formula $c = (\log a - x/a)/(\log b - y/b)$, is $c = 0.862$.

That *d*- α -phenylethylamine undergoes amide formation with *l*-quinic acid more slowly than the *l*-base was proved by heating together equivalent weights of *i*- α -phenylethylamine and *l*-quinic acid for 4½ hours at 165° and then recovering the residual base, which showed a marked dextrorotation. When this latter product was again submitted to fractional amide formation with *l*-quinic acid, the residual base had $\alpha_D + 3.5^\circ$ ($l = 1$).

The mixture of *l*-quinic acid-*l*-phenylethylamide and *l*-quinic acid-*d*-phenylethylamide formed contains an excess of the former, which is readily separated by crystallisation from water. *l*-Quinic acid-*l*-phenylethylamide melts at 220° and has $[\alpha]_D - 92.1^\circ$ ($c = 6.692$) in pyridine solution. When boiled with fuming hydrochloric acid, it forms *i*- α -chloroethylbenzene and *l*- α -phenylethylamine, which has d 0.9503 at 22°/4° and $[\alpha]_D - 39.51^\circ$ at 22°. Its rotation dispersion was also examined. Its hydrochloride melts at 171° and has $[\alpha]_D - 3.5^\circ$ ($c = 4$) in aqueous solution (compare Kipping and Hunter, *Trans.*, 1903, 83, 1147). No racemisation of the base had occurred during its formation from the amide.

The isolation of the *d*-base from the product, which had not been converted into amide during the fractional amide formation of the *i*-base with *l*-quinic acid, was effected by aid of the fact that the sulphate of the *i*-base is a *dl*-conglomerate and not an *r*-compound (compare *Abstr.*, 1899, i, 477). *d*- α -Phenylethylamine sulphate melts and decomposes at 272°. The free base has $[\alpha]_D + 39.66^\circ$; its carbamide melts at 122—123° and has $[\alpha]_D + 46.2^\circ$ ($c = 4.035$). By the action of sodium nitrate on the *l*-sulphate, a dextrorotatory phenylmethylcarbinol, having $[\alpha]_D + 2.7^\circ$, was obtained, during the formation of which optical inversion may have occurred.

The benzoyl derivative of *l*- α -phenylethylamine melts at 125.5°. Although practically inactive in ethyl-alcoholic solution, complete racemisation does not occur during its preparation by the Schotten-Baumann method, as is supposed by Kipping and Hunter (*loc. cit.*). The authors have determined its specific rotation in benzene, chloroform, propyl alcohol, ethyl alcohol, and methyl alcohol respectively.

A. McK.

Benzylethylaniline. ROBERT GNEHM (*J. pr. Chem.*, 1905, [ii], 71, 150—151).—Contrary to Schultz, Rohde, and Bosch's suggestion (*Abstr.*, 1904, i, 992), Gnehm and Scheutz (*Abstr.*, 1901, i, 519) did not make an exhaustive investigation of the action of nitric acid on benzylethylaniline.

G. Y.

Benzylethylaniline and Benzyldeneaniline. WILHELM VAUBEL and O. SCHEUER (*Zeit. Farb. Text. Ind.*, 1905, **4**, 88—89).—On brominating benzylethylaniline dissolved in glacial acetic acid by means of potassium bromide, potassium bromate, and hydrochloric acid, benzyl bromide and ethylaniline are first formed, the latter subsequently undergoing conversion into tribromoethylaniline. Benzyldeneaniline under similar treatment gives tribromoaniline. Both benzylethylaniline and benzyldeneaniline possess very feebly basic properties; even when small quantities of acid are added to large quantities of the bases either suspended in water or dissolved in ether, there is practically no formation of a salt. W. A. D.

Reaction between Tertiary Amines and Organo-magnesium Compounds. FRANZ SACHS and LUDWIG SACHS (*Ber.*, 1905, **38**, 1087—1088. Compare this vol., i, 190).—The discrepancies between the found and calculated molecular refractions for the tertiary amines, &c., recently described (this vol., ii, 190) disappear when Brühl's figures for C, H, &c., are employed instead of those given by Ostwald in calculating the theoretical values. E. F. A.

Lossen's Reaction. ERNST MOHR (*J. pr. Chem.*, 1905, [ii], **71**, 133—149. Compare Lossen, *Annalen*, 1875, **175**, 313; Thiele and Pickard, *Abstr.*, 1900, i, 29).—When warmed on the water-bath with concentrated alkali hydroxide, dibenzhydroxamic acid yields benzhydroxamic and benzoic acids with traces of aniline; with 1 mol. of an alkali hydroxide in dilute aqueous solution, the hydrolysis leads to the formation of diphenylcarbamide, carbon dioxide, benzoic acid, and small quantities of aniline, whilst with an excess of alkali hydroxide in 0.1*N*-aqueous solution the amount of diphenylcarbamide formed decreases, and that of the aniline increases, until with 3 mols. of alkali hydroxide only traces of the carbamide are obtained. The reaction is accompanied by an odour of phenylcarbylamine, which disappears on acidification.

The excess of dilute alkali hydroxide prevents the formation of diphenylcarbamide by accelerating the hydrolysis of the phenylcarbimide, first formed. In aqueous solution at 0°, phenylcarbimide is slowly converted into diphenylcarbamide, only traces of aniline being found in the solution, but with dilute potassium hydroxide at 0° phenylcarbimide is rapidly hydrolysed into aniline and carbon dioxide.

The formation of aniline in warm dilute alkali hydroxide solution may be used as a test for dibenzhydroxamic acid. G. Y.

Ethers and Esters of cycloHexanol. LÉON BRUNEL (*Bull. Soc. chim.*, 1905, [iii], **33**, 271—274. Compare *Abstr.*, 1903, i, 695, and 1904, i, 158).—The methyl and ethyl ethers were prepared either by the action of the appropriate alkyl iodide on the sodium derivative of cyclohexanol or by the reduction of the corresponding alkyl phenyl ethers.

cycloHexanyl methyl ether is a colourless, mobile liquid, which boils at 135.5°, has a sp. gr. 0.902 at 0°, and does not decolorise bromine or potassium permanganate. The ethyl ether resembles the foregoing, boils at 149.5°, has a sp. gr. 0.891 at 0°, and is slightly soluble in water, readily so in alcohol and ether.

cycloHexanyl formate, obtained by the action of formic acid on the alcohol, is a colourless, mobile liquid of agreeable odour; it boils at 162.5° and has a sp. gr. 1.010 at 0° . The *benzoate*, obtained by the action of benzoyl chloride on *cyclohexanol* in presence of pyridine, is a colourless, mobile, inodorous liquid, which boils at $192-193^{\circ}$ under 61 mm. pressure and has a sp. gr. 1.068 at 0° . *cycloHexanyl hydrogen succinate*, obtained by the action of succinic anhydride, alone and in excess, or in mol. proportion in presence of pyridine, on the alcohol, forms colourless crystals, melts at 44° , and is soluble in alcohol and ether. The normal *succinate*, obtained by the action of succinyl chloride on *cyclohexanol* in presence of pyridine, is a colourless, inodorous syrup. *cycloHexanyl hydrogen phthalate* separates from alcohol in large crystals and melts at 99° . The normal *ester* forms large, prismatic, colourless crystals and melts at 66° . T. A. H.

The Three Methylcyclohexanones and the Corresponding Methylcyclohexanols. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, 140, 350—352).—The three methylcyclohexanols are readily prepared by the direct hydrogenation of *o*-, *m*-, or *p*-cresol in the presence of reduced nickel at $200-220^{\circ}$ (compare Sabatier and Senderens, *Abstr.*, 1904, i, 156), and the ketones are obtained by the action of copper at 300° on the corresponding alcohols (compare Sabatier and Senderens, *Abstr.*, 1903, i, 454; 1904, i, 156). 1:2-Methylcyclohexanol, a colourless liquid boiling at $164.5-165.5^{\circ}$ under 745 mm. pressure, has a sp. gr. 0.9452 at $0^{\circ}/0^{\circ}$, its acetyl derivative has a fruity odour, boils at $181.5-182.5^{\circ}$ (corr.), and has a sp. gr. 0.968 at $0^{\circ}/0^{\circ}$; its phenylcarbamate forms brilliant prisms melting at 105° ; it yields two isomeric methylcyclohexenes on treatment with zinc chloride, one boiling at $108-109^{\circ}$ and having a sp. gr. 0.823 at $0^{\circ}/0^{\circ}$, the other boiling at $103-105^{\circ}$ and having a sp. gr. 0.821 at $0^{\circ}/0^{\circ}$. 1:2-Methylcyclohexanone is a colourless liquid boiling at $162-163^{\circ}$ (corr.), has a sp. gr. 0.9441 at $0^{\circ}/0^{\circ}$, and its semicarbazone melts at 191° .

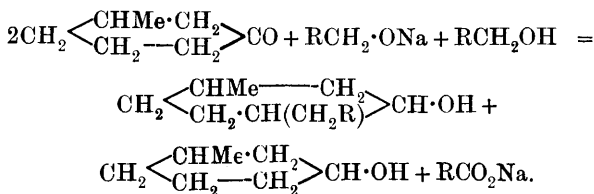
1:3-Methylcyclohexanol is a colourless liquid boiling at 172.5° under 745 mm. pressure, has a sp. gr. 0.9336 at $0^{\circ}/0^{\circ}$; its acetyl derivative boils at 185.5° (corr.) and has a sp. gr. 0.960 at $0^{\circ}/0^{\circ}$; its phenylurethane forms large, thick crystals melting at 96° and on treatment with zinc chloride it yields a methylcyclohexene, boiling at 105° (corr.), and having a sp. gr. 0.819 at $0^{\circ}/0^{\circ}$ (compare Markownikoff, *Abstr.*, 1900, i, 579).

1:3-Methylcyclohexanone is a colourless liquid, boiling at 169° under 765 mm. pressure, has a sp. gr. 0.9330 at $0^{\circ}/0^{\circ}$ and yields a semicarbazone, crystallising from methyl alcohol in rhombic plates melting at 182.5° .

1:4-Methylcyclohexanol is a colourless, viscous liquid boiling at $172.5-173^{\circ}$ under 745 mm. pressure, has a sp. gr. 0.9328 at $0^{\circ}/0^{\circ}$, forms a phenylcarbamate crystallising in brilliant prisms and melting at 125° , and on treatment with zinc chloride yields the same methylcyclohexene as that yielded under similar conditions by the 1:3-isomeride. 1:4-Methylcyclohexanone boils at 169.5° , has a sp. gr. 0.9332 at $0^{\circ}/0^{\circ}$, and forms a semicarbazone which crystallises from alcohol in thick,

oblique prisms melting at 197° (compare Einhorn, Abstr., 1897, i, 345). M. A. W.

A New Method of Synthesising Alkyl Derivatives of Certain Saturated Cyclic Alcohols. Preparation of Homologues of Menthol. ALBIN HALLER and FRANÇOIS MARCH (*Compt. rend.*, 1905, 140, 474—479).—Haller has already shown that camphor reacts with the sodium alkyl oxides to form the corresponding alkyl derivative of camphor and of borneol (compare Abstr., 1892, 72), and an extension of the investigation to other cyclic ketones shows that methyl-3-cyclohexanone reacts with the sodium alkyl oxides at 220—225° in an autoclave to form the 1-methyl-4-alkyl-3-cyclohexanol, 1:3-methylcyclohexanol, and the sodium salt of the acid corresponding with the alcohol employed, according to the equation :



The phenols thus obtained were identical with those prepared by reducing the corresponding 1-methyl-4-alkyl-3-cyclohexanones (compare this vol., i, 214). 1-Methyl-4-propyl-3-cyclohexanol boils at 111—113° under 23 mm. pressure, has a sp. gr. 0.9105 at 0°/4° or 0.8976 at 19°/4°, $[\alpha]_D - 18^\circ$ at 19°, and forms a *phenylcarbamate*, which crystallises in long, thin needles melting at 108—109°. 1-Methyl-4-isobutyl-3-cyclohexanol, melting at 68—69°, has $[\alpha]_D - 70^\circ 22'$, and forms a crystalline *phenylcarbamate* melting at 77°; the liquid stereoisomeride, boiling at 110—111° under 16 mm. pressure, has $[\alpha]_D - 18^\circ 8'$ to $-22^\circ 11'$. 1-Methyl-4-isoamyl-3-cyclohexanol boils at 137° under 23—24 mm. pressure, has a sp. gr. 0.9000 at 0°/4° or 0.8909 at 20°/4°, and $[\alpha]_D - 24^\circ 28'$, and does not form a crystalline phenylcarbamate. M. A. W.

4-Benzyl-1-methyl-3-cyclohexanol and 2:4-Dibenzyl-1-methyl-3-cyclohexanol. ALBIN HALLER and FRANÇOIS MARCH (*Compt. rend.*, 1905, 140, 624—629).—When 1-methyl-3-cyclohexanone is heated at 220—225° for 24 hours with benzyl alcohol in which sodium has been dissolved, a mixture of 4-benzyl-1-methyl-3-cyclohexanol and 2:4-dibenzyl-1-methyl-3-cyclohexanol is obtained. On distillation under 21 mm. pressure, a considerable fraction can be collected between 180° and 187° and a second fraction between 240° and 265°.

From the first fraction, two products are obtained, both of which correspond with the formula $\text{C}_{14}\text{H}_{20}\text{O}$. The first melts at 101.5—102° and has $[\alpha]_D - 53^\circ 21'$ in absolute alcohol. The second melts at 79—80°. The two substances are in all probability stereoisomeric forms of 4-benzyl-1-methyl-3-cyclohexanol. The first of these is identical with the substance obtained by Wallach (Abstr., 1897, i, 159) by reduction of 4-benzylidene-1-methyl-3-cyclohexanone by means of

sodium ethoxide in ethyl alcohol. It is also obtained by boiling 1-methyl-3-*cyclohexanol* with sodium in presence of toluene and adding benzaldehyde in small portions at a time to the boiling mixture.

On redistillation, the main portion of the second fraction passes over at 257—258°. The product thus obtained is 2:4-dibenzyl-1-methyl-3-*cyclohexanol* and has $[\alpha]_D - 10.5'$ in absolute alcohol.

The results indicate that methyl*cyclohexanone* behaves differently from camphor when reduced at high temperatures with sodium in benzyl alcohol solution. In the case of camphor, the only action is one of substitution, but with methyl*cyclohexanone* reduction also takes place.

H. M. D.

Tribromophenol Bromide: its Detection, Estimation, Rate of Formation, and Reaction with Hydriodic Acid. S. J. LLOYD (*J. Amer. Chem. Soc.*, 1905, 27, 7—15).—Ammonia and many organic bases react with tribromophenol bromide with formation of coloured substances. These reactions are of value for the detection of the compound. When a solution of aniline or benzidine in chloroform is added to a solution containing tribromophenol bromide, a coloration is produced which is deep red in the case of the former reagent and intense green (or purple if concentrated) in the case of the latter.

The estimation of tribromophenol bromide may be effected by reducing the compound with zinc dust and sulphuric acid and determining the amount of hydrogen bromide formed.

The formation of tribromophenol bromide when phenol is treated with bromine water is due to the gradual action of the excess of bromine water on the tribromophenol which is first produced. Experiments were made to determine the amount of tribromophenol bromide formed when bromine reacts with phenol under varying conditions. It is found that the amount of tribromophenol bromide produced increases with the time during which the bromine is left in contact with the tribromophenol, although under ordinary conditions a considerable quantity may be formed in a few minutes. The results also show that in order to avoid the formation of tribromophenol bromide in the titration of phenol with bromine, the liquid must be strongly acid or must contain an excess of potassium bromide; a large excess of bromine must not be employed, and the precipitated tribromophenol must not be left too long with the excess of bromine water. Since the rate of formation of tribromophenol bromide is decreased by the addition of acid or potassium bromide, and increased by adding water or bromine or by raising the temperature, the conclusion is drawn that the action is due to the presence of hypobromous acid in the bromine water.

Tribromophenol bromide is not reduced quantitatively to tribromophenol by hydriodic acid under ordinary conditions, but is partially converted into other products.

E. G.

Trinitroveratrole. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 462—465).—When 3:5-dinitroveratrole is nitrated, the nitro-group is introduced between the two existing nitro-groups; the trinitroveratrole formed is thus 3:4:5-nitro-1:2-di-

methoxybenzene, and is identical with the substance formed by the nitration of 3:5-dinitrocatechol dimethyl ether.

By interaction of alcoholic ammonia and trinitroveratrole, ammonium nitrite is formed together with 3:5-dinitro-2:4-diamino-1-methoxybenzene, which melts at 247° and is identical with the compound formed by the action of alcoholic ammonia on trinitroquinol dimethyl ether. When trinitroquinol dimethyl ether is treated with sodium methoxide, 3:5-dinitro-1:2:4-trimethoxybenzene, melting at 92°, is produced, and this, when treated with alcoholic ammonia, gives the same dinitro-diaminoanisole as was obtained from trinitroquinol dimethyl ether. The behaviour of trinitroveratrole with sodium methoxide is different, yellow crystals of a *compound* melting at 152°, and not affected by alcoholic ammonia, being obtained.

A. McK.

Benzylphenyl Salicylate. VINCENZO MAJONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iiia], 10, 393—394).—*Benzylphenyl salicylate*, $C_7H_5O_2 \cdot O \cdot C_6H_4 \cdot CH_2Ph$, obtained by the interaction of benzylphenol and salicylic acid in benzene solution in presence of phosphoric oxide, separates from alcohol in crystals melting at 90—91°, and dissolves in chloroform, acetone, benzene, or ether, and to a slight extent in light petroleum.

T. H. P.

Action of Organo-magnesium Compounds on Doubly Unsaturated Ketones. HUGO BAUER (*Ber.*, 1905, 38, 688—690).—*αεζ-Triphenyl-Δ^{αγ}-hexadiene-ε-ol*, $CHPh:CH:CH:CH \cdot CPh(OH) \cdot CH_2Ph$, prepared from cinnamylideneacetophenone and magnesium benzyl chloride, forms colourless needles and melts at 124—125°. *αε-Diphenyl-Δ^{αγ}-heptadiene-ε-ol*, $CHPh:CH:CH:CH \cdot CPh(OH) \cdot CH_2 \cdot CH_3$, obtained from cinnamylideneacetophenone and magnesium ethyl iodide, crystallises from alcohol in colourless needles and melts at 76°. *αζ-Diphenyl-ε-methyl-Δ^{αγ}-hexatriene*, $CHPh:CH:CH:CH \cdot CMe:CHPh$, formed by the interaction of less than 1 mol. of cinnamylideneacetone with 1 mol. of magnesium benzyl chloride in ethereal solution, crystallises from alcohol in fluorescent leaflets and melts at 115—116°.

W. A. D.

Decahydro-β-naphthol and Octahydronaphthalene. HENRI LEROUX (*Compt. rend.*, 1905, 140, 590—591. Compare Abstr., 1904, i, 986).—Decahydro-β-naphthol, $C_{10}H_{17} \cdot OH$, obtained by repeated hydrogenation of β-naphthol below 200°, crystallises from petroleum in colourless needles melting at 75°, boils at 115° under 13 mm. pressure, or at 230° with decomposition under the ordinary pressure, is slightly soluble in water, readily so in alcohol, benzene, ether, or carbon bisulphide, and is volatile in steam; the *acetyl* derivative, $C_{10}H_{17} \cdot OAc$, obtained by the prolonged action of acetic anhydride at 130°, is a colourless liquid with a fruity odour, boiling at 120° under 12 mm. or at 250° under the ordinary pressure; the *phenylcarbamate*, $NHPh \cdot CO \cdot OC_{10}H_{17}$, crystallises from light petroleum in thin, white needles melting at 165° and subliming at 160°. *Octahydronaphthalene*, $C_{10}H_{16}$, obtained when decahydro-β-naphthol is heated with potassium hydrogen sulphate, is a

liquid boiling at 190° (corr.) and having a sp. gr. 0.910 to 0.9009 at 13° ; it unites directly with bromine to form *dibromo-octahydronaphthalene*, $C_{10}H_{16}Br_2$, which crystallises from alcohol in small, colourless prisms melting at 85° , readily soluble in chloroform, ether, or petroleum, and less so in alcohol or acetone. M. A. W.

Unsaturated Compounds. II. Addition of Mercaptans to Unsaturated Hydrocarbons. THEODOR POSNER [with J. S. TSCHARNO] (*Ber.*, 1905, **38**, 646—657).—Sulphides or sulphones could not be obtained from ethylene or propylene or from stilbene or diphenylbutadiene; trimethylethylene and amylene react with thiophenol or benzyl mercaptan, but not with ethyl mercaptan. *Phenyl- α - β -dimethylpropylsulphone*, $CHMe_2 \cdot CHMe \cdot SO_2Ph$, prepared from trimethylethylene and thiophenol, crystallises in colourless plates melting at 32° ; dimethylethylcarbinol bromide and sodium benzylsulphinat react forming the isomeric *phenyl- α -dimethylpropylsulphone*, $CMe_2Et \cdot SO_2Ph$, which separates in colourless prisms melting at 70° . *Benzyl- α - β -dimethylpropylsulphone*, $CHMe_2 \cdot CHMe \cdot SO_2 \cdot C_7H_7$, forms needles melting at 58 — 59° .

Phenyl- β -phenylethylsulphone, $CH_2Ph \cdot CH_2 \cdot SO_2Ph$, prepared from styrene and thiophenol, forms colourless plates which melt at 58° ; the isomeric *phenyl- α -methylbenzylsulphone*, $CHPhMe \cdot SO_2Ph$, crystallises in colourless cubes melting at 115° . *Phenyl- β -phenylpropylsulphone*, $CHPhMe \cdot CH_2 \cdot SO_2Ph$, separates in colourless plates melting at 94° ; *benzyl- β -phenylpropylsulphone*, $CHPhMe \cdot CH_2 \cdot SO_2 \cdot CH_2Ph$, forms plates melting at 163° .

From pinene and benzyl mercaptan, as also from sabinene and thiophenol, only oils were obtained; camphene and benzyl mercaptan yielded *dihydrocamphene- β -benzylsulphone*, $C_7H_{12} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CH \cdot CH_2 \cdot SO_2 \cdot C_7H_7 \end{smallmatrix}$, which separates from alcohol in plates melting at 127° ; the corresponding *dihydrocamphene- β -phenylsulphone*, $C_7H_{12} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CH \cdot CH_2 \cdot SO_2Ph \end{smallmatrix}$, crystallises in plates and melts at 73° . The isomeric *dihydrocamphene- α -phenylsulphone*, $C_7H_{12} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CMe \cdot SO_2Ph \end{smallmatrix}$, melts at 75° , whilst a mixture of the α - and β -derivatives melts at 60° .

Tetrahydronaphthalenephennylsulphone, $C_{10}H_8 \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ CH_2 \cdot CH \cdot SO_2Ph \end{smallmatrix}$, separates from alcohol in plates and melts at 139° ; *dihydromenthene- β -phenylsulphone*, $C_{10}H_{16}MePr^{\beta} \cdot SO_2Ph$, was obtained and analysed as a yellow oil. *Phenyl- δ -phenylbutenylsulphone*, $CHPh \cdot CH \cdot CH_2 \cdot CH_2 \cdot SO_2Ph$, melts at 111° . *cyclopentanediphenyldisulphone*, $C_5H_8(SO_2Ph)_2$, was obtained in the form of colourless needles melting at 232 — 233° . From terpinene, terpinolene, sylvestrene or cedrene and thiophenol, oils were obtained corresponding in composition with additive products containing one molecule of the mercaptan. Crystallised acetates could not be prepared from these. *Tetrahydrolimonenediphenyldisulphone* crystallises in needles which melt and decompose at 236 — 237° . E. F. A.

The Ring System of Benzene. VII. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1905, 38, 789—793. Compare Abstr., 1900, i, 480; 1901, i, 318; 1903, i, 19; 1904, i, 690).—It has already been shown that the carbethoxyl group acts as a fluorogen, and it is now shown that the acetyl and vinyl groups act in the same manner when introduced into the molecule of quinol dimethyl ether.

2:5-Dimethoxyacetophenone (Klages, Abstr., 1904, i, 1003) forms prismatic crystals melting at 20—22°, and in alcoholic solutions exhibits strong fluorescence. The *phenylhydrazone*, $C_{16}H_{18}O_2N_2$, crystallises in yellow prisms, melts at 99—100°, and is not stable in contact with the air; it does not fluoresce. A by-product melting at 50—51° and probably the monomethyl ether of quinacetophenone is obtained in the preparation of the dimethoxy-compound.

2:5-Dimethoxy-1- α -methylvinylbenzene (Klages, Abstr., 1904, i, 1004) may be obtained by distilling the corresponding carbinol under atmospheric pressure. Its vapour luminesces under the influence of Tesla rays, and its alcoholic solutions are fluorescent.

The quinol dimethyl ether and its two derivatives have anomalous molecular refractions. The two derivatives do not fluoresce in associating solvents. In methyl or ethyl alcohol, they possess only a feeble violet fluorescence, in *isobutyl* alcohol the fluorescence is most pronounced, and in *benzyl* alcohol the fluorescence is marked, but of a bluer shade. The temperature-coefficient of the fluorescence is also very considerable.

2:5-Dimethoxy-1- $\alpha\beta$ -dimethylvinylbenzene, $C_6H_3(OMe)_3 \cdot CMe:CHMe$, boiling at 254—255°, and dimethoxy- α -methylstilbene are also fluorescent. J. J. S.

The Ring System of Benzene. VIII. HUGO KAUFFMANN and AD. GROMBACH (*Ber.*, 1905, 38, 794—801. Compare preceding abstract).—Benzoyl and other substituents have been introduced into the molecule of quinol dimethyl ether and the products investigated as regards their luminescence in presence of radium bromide, and also as regards their fluorescence. The following summary is given, where a = no. of cm. between the substance and 5 mg. of radium bromide when luminescence is just visible, b = distance when a sheet of zinc foil 0.75 mm. thick is interposed, and X = the substituent.

Quinol dimethyl ether, $a = 9.3$, $b = 1.0$; X = $CPh(OH)(CH_2Ph)$, $a = 6.5$, $b = 0.3$; X = $COPh$, $a = 11.7$, $b = 1.0$; X = $CEtPh \cdot OH$, $a = 13.0$, $b = 1.6$; X = $CPhN:NHPh$, $a = 13.0$, $b = 1.5$; X = $CPh:CHPh$, $a > 13.0$, $b = 4.9$; X = $CPh_2 \cdot OH$, $a > 13.0$, $b = 5.4$.

None of the compounds fluoresces, and it is obvious that substituents which increase the luminescence to an enormous degree need not necessarily function as "fluorogens."

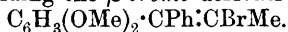
Benzoylquinol dimethyl ether (2:5-methoxybenzophenone),



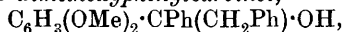
obtained by the Friedel-Craft synthesis, crystallises from light petroleum in pale yellow crystals, melts at 51°, distils at 225° under 30 mm. pressure, is readily soluble in most organic solvents, and is coloured a reddish-brown by concentrated sulphuric acid. The *phenylhydrazone* melts at 125°, the *monomethyl ether*, $OH \cdot C_6H_3(OMe) \cdot COPh$, melts at 78°.

Phenyl-2:5-dimethoxyphenylethylcarbinol, $C_6H_3(OMe)_2 \cdot CEtPh \cdot OH$, obtained by the Grignard synthesis, forms large, clear crystals, melts at 56° , boils at 230° under 30 mm. pressure, and is readily soluble in the usual organic solvents with the exception of alcohol and light petroleum. With concentrated sulphuric or syrupy phosphoric acid, it gives a dark blue coloration.

α -Phenyl- α -2:5-dimethoxyphenylpropylene, $C_6H_3(OMe)_2 \cdot CPh \cdot CHMe$, obtained by the action of hydrogen chloride on the carbinol and subsequent distillation, is a colourless liquid distilling at 198° under 12 mm. pressure. It forms an unstable *dibromide*, which readily loses hydrogen bromide yielding the β -bromo-derivative,



Phenylbenzyl-2:5-dimethoxyphenylcarbinol,



crystallises in long, colourless needles, melts at 110° , and is readily soluble in carbon disulphide, chloroform, or benzene.

2:5-Dimethoxy- α -phenylstilbene, $C_6H_3(OMe)_2 \cdot CPh \cdot CHPh$, obtained from the carbinol by means of hydrogen chloride, crystallises from light petroleum in large prisms melting at 82.5° ; it yields an unstable oily *dibromide*, which readily loses hydrogen bromide, yielding a *monobromo-derivative*, $C_{22}H_{19}O_2Br$, melting at 118° .

Diphenyl-2:5-dimethoxyphenylcarbinol, $C_6H_3(OMe)_2 \cdot CPh_2 \cdot OH$, melts at 141° and is only sparingly soluble in alcohol or light petroleum.

J. J. S.

Dibenzylideneacetone and Triphenylmethane. VII. ADOLF VON BAEYER (*Ber.*, 1905, **38**, 569—590. Compare *Abstr.*, 1902, i, 380, 769; 1903, i, 811; 1904, i, 308, 786, 898).—The halogen derivatives of triphenylcarbinol have been examined in order to prove that they do not possess the quinonoid structure. It had already been shown by Baeyer and Villiger that certain coloured derivatives of triphenylcarbinol cannot be represented as having this structure.

p-Trichloro- and *p*-tri-iodo-triphenylcarbinol form with concentrated sulphuric acid coloured salts, which, in contact with silver acetate, do not form silver chloride, as they would do if they were quinonoid in structure. The chromophore group in those salts is accordingly identical with that of triphenylcarbinol, the halogen atoms acting as auxochrome groups.

The basic properties of carbon are discussed. Carbon differs from other elements, which form "onium" bases, in that it forms salts only, the free base either not existing at all or being very unstable. The basic properties of carbon are shown in the coloured salts of triphenylmethyl. From the experiments of Walden and of Gomberg, who have shown that colourless derivatives of triphenylmethyl form a yellow solution with strongly dissociated solvents and that such solutions conduct electricity, the conclusion is drawn that one and the same compound can exist in two forms, a colourless one, which does not undergo electrolytic dissociation, and a coloured one, which does. The possibility of the existence of two triphenylcarbinols having the same composition and the same structural formula, but one of them being a strong coloured base and the other an indifferent colourless substance, is considered, as also is the possibility of existence of two

rosanilines, one coloured and basic and the other colourless and indifferent.

The distinction is drawn between an ionisable and a non-ionisable valency; the former is termed a "carbonium valency" and is indicated by a waved line, thus: $\text{CPh}_3 \cdot \text{OH} + \text{H}_2\text{SO}_4 = \text{Ph}_3\text{C} \cdots \text{O} \cdot \text{SO}_3\text{H} + \text{H}_2\text{O}$.

The carbonium isomerism of phthaleins is discussed. The author does not consider that Werner's carboxonium salts contain quadri-valent oxygen, as supposed by Werner; they are regarded as carbonium salts, corresponding with the salts of triphenylmethyl.

Thus the salt formulated by Werner as $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{Br} \end{smallmatrix} \text{C}_6\text{H}_4$ is formulated by the author as $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4 \text{Br}$.

The colour in fulvene derivatives, in fuchsone and fuchsoneimine, and in aurin is due to the double linking, which is designated as a "carbonium double linking."

The paper also includes a discussion of triphenylmethyl derivatives which contain nitrogen; the formation of magenta from rosaniline; the action of alkali on magenta and on crystal-violet; the constitution of Homolka's base (diaminofuchsoneimine) and of dibenzylideneacetone, and the nature of azonium compounds.

p-Trichlorotriphenylcarbinol, prepared from *p*-chloriodobenzene and methyl *p*-chlorobenzoate by means of Grignard's reaction, separates from light petroleum in needles or prisms and melts at 98—99°. It differs from triphenylcarbinol by being less basic, by the redder colour of its solutions and by the greater ease with which its sulphate crystallises. The sulphate forms brown, metallic prisms, which are immediately decomposed by water. When silver acetate is added to a solution of the sulphate in glacial acetic acid, silver chloride is not produced. When trichlorotriphenylcarbinol is warmed with a mixture of aniline hydrochloride and aniline, and the aniline then expelled by addition of sodium hydroxide and distillation in steam, the addition of picric acid to the benzene solution of the product gives the reaction characteristic of triphenylrosaniline.

p-Trichlorotriphenylmethyl chloride, $\text{C}_{19}\text{H}_{12}\text{Cl}_3 \cdot \text{Cl}$, prepared by the action of acetyl chloride on *p*-trichlorotriphenylcarbinol, separates from light petroleum in glistening, colourless needles and melts at 113°. The stannichloride forms red crystals resembling chromic acid.

p-Tri-iodotriphenylcarbinol, prepared by the replacement of the three amino-groups in pararosaniline by iodine by Knoevenagel's method, separates from methyl alcohol in needles or prisms containing methyl alcohol of crystallisation, and from a mixture of ether and formic acid in colourless, quadratic plates, and melts at 162—163°. Its sulphate forms glistening, green crystals and does not yield silver iodide when acted on by silver nitrate.

p-Tri-iodotriphenylmethyl chloride separates from a mixture of light petroleum and chloroform in glistening prisms and melts and decomposes at 180°.

A. McK.

Anethoglycol [γ -*p*-Methoxyphenylpropane- β -diol]. EUGÈNE VARENNE and L. GODEFROY (*Compt. rend.*, 1905, 140, 591—593).—The

glycol of anethol (γ -p-methoxyphenylpropane- $\beta\gamma$ -diol),
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{OH}$,

prepared by the action of alcoholic potassium hydroxide on dibromoanethole at the ordinary temperature, is a viscid, amber-coloured liquid possessing an aromatic and a sweet taste, having a sp. gr. 1.013 at 17° and boiling at 245—250°. The *monoacetate* is obtained by the action of acetic and hydrochloric acids on the glycol, and the *diacetate* by the action of acetyl chloride. M. A. W.

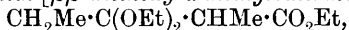
New Syntheses [of Esters] with Magnesium Organo-compounds. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1905, **38**, 561—566).—The author describes several new applications of Grignard's reaction. When magnesium alkyl haloids act on normal carbonic esters, the main reaction is represented by the equation $\text{RMgX} + \text{CO}(\text{OEt})_2 = \text{R}\cdot\text{C}(\text{OMgX})(\text{OEt})_2$. By the action of water on the compound obtained, an ester is formed, thus: $\text{R}\cdot\text{C}(\text{OMgX})(\text{OEt})_2 + \text{H}_2\text{O} = \text{R}\cdot\text{CO}_2\text{Et} + \text{EtOH} + \text{MgX}\cdot\text{OH}$. The yield of ester by this method is sometimes as much as 80 per cent. of the theoretical, whilst tertiary alcohols are formed to a very slight extent only.

Ethyl benzoate was prepared by the action of magnesium phenyl bromide on ethyl carbonate, ethyl *isohexoate* by the action of magnesium *isoamyl* bromide on ethyl carbonate, and ethyl hexahydrobenzoate by the action of magnesium *cyclohexyl* chloride on ethyl carbonate. The action of magnesium on the alkyl haloids was conducted in each case in an atmosphere of hydrogen.

If the reaction between magnesium organo-compounds and ortho-carbonic esters be moderated and not too prolonged, it proceeds thus: $\text{C}(\text{OEt})_4 + \text{R}\cdot\text{MgX} = \text{R}\cdot\text{C}(\text{OEt})_3 + \text{MgX}(\text{OEt})$. Tertiary alcohols are, however, formed in small amounts.

Ethyl orthobenzoate, prepared by the action of magnesium phenyl bromide on ethyl orthocarbonate, boils at 238—240° under 747 mm. pressure (Limpricht gives 220—225°), and has a sp. gr. 0.9902 at 20°/0°.

Ethyl orthopropionate, formed by the action of magnesium ethyl iodide on ethyl orthocarbonate, was not separated from the product of the reaction owing to the proximity of its boiling point with that of ethyl orthocarbonate. When the reaction was allowed to proceed vigorously, three fractions were obtained, the first containing ethyl propionate, the second ethyl orthopropionate, and the third *ethyl propionylpropionate acetal* [$\beta\beta$ -diethoxy- α -methylvalerate],



which boils at 223—226°. A 5 per cent. solution of hydrogen chloride converts it into ethyl propionylpropionate, from which diethyl ketone is prepared by hydrolysis with alkali. A. McK.

Condensation of Benzyl Chloride with the Aminobenzoic Acids. GIUSEPPE KERNOT and E. PETRONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iia], **10**, 382—392).—Condensation of benzyl chloride with anthranilic acid in 96 per cent. alcoholic solution in presence of zinc yields the benzylanthranilic acid obtained by Henze (*Abstr.*, 1899, i, 218). The *phenyl* ester, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Ph}$, separates from alcohol in tufts of pale yellow, prismatic crystals melt-

ing at 74—75°; the *p*-tolyl ester, $C_7H_7 \cdot NH \cdot C_6H_4 \cdot CO_2 \cdot C_6H_4Me$, forms prismatic needles melting at 79—80°, the *m*-tolyl ester, tufts of colourless, prismatic crystals which turn yellow on exposure to light, and the *o*-tolyl ester, minute crystals; the β -naphthyl ester forms mammillary masses of minute, white or pale yellow needles melting at 91—92°, and the α -naphthyl ester crystals melting at 76—77°.

Benzylanthranil, $C_6H_4 \cdot \begin{smallmatrix} N \cdot C_7H_7 \\ | \\ CO \end{smallmatrix}$, prepared by the action of phosphorus oxychloride on benzylanthranilic acid in toluene solution, crystallises from alcohol in tufts of monoclinic prisms [$a:b:c = 1.2695:1:1.0337$; $\beta = 57^\circ 29'$], melting at 153.5—154°, and is soluble in the ordinary organic solvents.

The constitution of anthranil and its derivatives is discussed.

T. H. P.

Syntheses of Arylnitromethanes and of Stilbene Derivatives. WILHELM WISLICENUS and HENRY WREN (*Ber.*, 1905, **38**, 502—510).—The reactions previously described for the preparation of phenylisonitromethane and of stilbene (*Abstr.*, 1902, i, 541) are now shown to be of general application.

o-Tolylacetonitrile (*Abstr.*, 1885, 889), sodium ethoxide, and ethyl nitrate yield sodium *o*-tolylisonitroacetonitrile, $C_6H_4Me \cdot C(CN):NO \cdot ONa$, which dissolves in water to a colourless, neutral solution; when acidified at 0°, it yields the tolylisonitroacetonitrile as a white precipitate, which gives a red coloration with ferric chloride. It is extremely unstable and is readily transformed into a red resin.

o-Tolynitromethane, $C_6H_4Me \cdot CH_2 \cdot NO_2$ (Goldberg, *Abstr.*, 1901, i, 33), is obtained when the sodium derivative is boiled for some time with aqueous sodium hydroxide, but when more concentrated alkali and a higher temperature (200°) are employed a good yield of *o*-dimethylstilbene is obtained. This crystallises from methyl alcohol in flat, colourless needles melting at 82.5—83°. The *picrate* forms red needles melting at 102—103°.

Sodium *m*-tolylisonitroacetonitrile crystallises readily from absolute alcohol, and with alkali yields *m*-tolynitromethane (Heilmann, *Abstr.*, 1891, 201) or *m*-dimethylstilbene, the *picrate* of which melts at 96.5—97.5°. The *p*-dimethylstilbene has been prepared in a similar manner.

α -Naphthylmethyl chloride (Scherler, *Abstr.*, 1892, 493) is best prepared by leading chlorine into α -methylnaphthalene at 250° until the increase in weight is 50 per cent. of the theoretical, and subsequent fractionation. The corresponding *nitrile* is an oil distilling at 191—194°. Sodium α -naphthylisonitroacetonitrile appears to have the composition $C_{10}H_7 \cdot C(CN):NO \cdot ONa, H_2O$. When boiled with dilute sodium hydroxide and acidified, it yields α -naphthylnitroacetamide, $C_{10}H_7 \cdot CH(NO_2) \cdot CO \cdot NH_2$, melting at 155—156°. With more concentrated alkali, it yields α -naphthylnitromethane, which crystallises from light petroleum in yellow needles melting at 72—73°. With sodium hydroxide at 150—160°, α -dinaphthastilbene (Elbs, *Abstr.*, 1893, i, 271) is formed.

β-Naphthylnitromethane dissolves readily in all organic solvents and melts at about 72°. *β-Dinaphthastilbene* crystallises from benzene in colourless plates melting at 254—255°.

The nitro-compounds give Gabriel's reaction.

J. J. S.

Elimination of Carbon Monoxide from Tertiary Acids with Concentrated Sulphuric Acid. II. AUGUSTIN BISTRZYCKI and EUGEN REINTKE (*Ber.*, 1905, 38, 839—848).—*αα*-Ditolylpropionic acid, when shaken in the cold with concentrated sulphuric acid, loses carbon monoxide and is converted into *as*-di-*p*-tolylethylene, $C(C_7H_7)_2 \cdot CH_2$, crystallising in colourless, glistening plates which melts at 61° and is identical with the ditolylethylene obtained as an oil by Hepp (this Journal, 1875, 361). Both products yielded the di-*p*-tolyl ketone melting at 95°, which forms a *phenylhydrazone* crystallising in aggregates of short, yellow prisms and melting at 100°.

αα-Di-*o*-xylylpropionic acid, $CMe(C_6H_3Me_2) \cdot CO_2H$, prepared by the condensation of *o*-xylene and pyruvic acid in concentrated sulphuric acid at -10°, crystallises in colourless, flat prisms arranged in concentric clusters, melts at 149°, and forms a crystalline *barium* salt. *as*-Di-*o*-xylylethylene, $C(C_6H_3Me_2)_2 \cdot CH_2$, melts at 73—74° and is easily oxidised to 3:4:3':4'-tetramethylbenzophenone, $CO(C_6H_3Me_2)_2$; this melts at 140°, forms an *oxime* crystallising in prisms and melting at 147°, and a *phenylhydrazone* melting at 130°.

2:5-Dimethylatropic acid, $CH_2 \cdot C(C_6H_3Me_2) \cdot CO_2H$, prepared from *p*-xylene and pyruvic acid, forms colourless, rhombic plates melting at 130—131°. Carbon monoxide is eliminated by concentrated sulphuric acid from this at 110—120°. *Dimethylatropic acid dibromide*, prepared by brominating the acid in carbon bisulphide solution, crystallises in colourless, short prisms melting at 153°, with elimination of hydrogen bromide.

2:5-Dimethyldihydroatropic acid, $C_6H_3Me_2 \cdot CHMe \cdot CO_2H$, prepared by reducing dimethylatropic acid with sodium amalgam, crystallises in colourless needles and melts at 115—116°.

αα-Di-*m*-xylylpropionic acid crystallises in six-sided, pointed prisms and melts at 168—169°.

E. F. A.

Conversion of *allo*Cinnamic Acid into Erlenmeyer's *iso*-Cinnamic Acid. EMIL ERLENMEYER, jun. (*Ber.*, 1905, 38, 837—838. Compare *Abstr.*, 1896, i, 46; 1904, i, 892).—Both Liebermann (*Abstr.*, 1898, i, 662) and Michael (*Abstr.*, 1902, i, 32) have been unable to convert *allocinnamic* into *isocinnamic* acid. The author has repeated Erlenmeyer's experiments, and finds that 0.5 gram of *allocinnamic* acid, dissolved in alcohol in presence of zinc bromide and kept in the dark during six days, is converted into the characteristic crystals of *isocinnamic* acid.

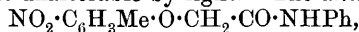
E. F. A.

Transformation of Racemic Compounds into the Corresponding Optically Active Forms. WILLY MARCKWALD and DAVID M. PAUL (*Ber.*, 1905, 38, 810—812).—When an optically active compound with one asymmetric carbon acid is racemised by

heat, equilibrium is established when equal amounts of the two mirror images are present. The case is, however, different in the racemisation by heat of a compound containing two asymmetric carbon atoms, and where interchange of groups takes place only at one of the carbon atoms.

r-Mandelic acid was heated for 10 hours at 150–160° with the amount of anhydrous brucine requisite for the formation of the brucine salt. The product was then dissolved in water, acidified by sulphuric acid, and extracted with ether, when the mandelic acid obtained was found to be feebly dextrorotatory. From this mixture of *d*- and *r*-acids, pure *d*-mandelic acid was isolated by Marckwald and McKenzie's method (Abstr., 1899, ii, 733). A. McK.

Nitrotolylglycollic [Nitrotolylxyacetic] Acids. GIUSEPPE KERNOT (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1904, [iiia], 10, 373–381).—The action of concentrated nitric acid of sp. gr. 1.4 on *p*-tolylglycollic acid yields a nitrocresol melting at 77° and 3-nitro-*p*-tolylxyacetic acid, $C_9H_5O_5N$ [$O\cdot CH_2\cdot CO_2H : NO_2 : Me = 1 : 3 : 4$], which may also be obtained by the interaction of 3-nitro-*p*-cresol and ethyl chloroacetate, and separates from aqueous alcohol in shining, yellow, flattened needles melting at 140–141°; it is slightly soluble in water, more so in benzene or chloroform, and readily so in alcohol or ether. The barium salt [with $3H_2O$] forms aggregates of orange-yellow prisms and the silver salt separates from water in aggregates of pale yellow, silky needles almost unalterable by light. The anilide,



crystallises from alcohol in pale yellow, flattened prisms and from benzene in well-defined, rhombic plates melting at 134°. On reduction in alcoholic solution by means of tin and hydrochloric acid, it yields 3-amino-*p*-tolylxyacetic acid, $C_9H_{11}O_3N$ [$O\cdot CH_2\cdot CO_2H : NH_2 : Me = 1 : 3 : 4$], which crystallises from water in white plates, melts at 200°, changes slowly in the light, and is soluble in alcohol or benzene.

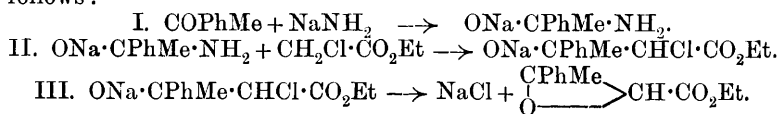
The action of nitric acid on *o*-tolylxyacetic acid yields a mixture of various nitro-derivatives, together with 6-nitro-*o*-tolylxyacetic acid [$O\cdot CH_2\cdot CO_2H : NO_2 : Me = 1 : 6 : 2$], which may also be obtained by the interaction of 6-nitro-*o*-cresol [$Me : OH : NO_2 = 1 : 2 : 6$] and ethyl chloroacetate, and crystallises from aqueous alcohol in shining, yellow needles softening at 128° and melting at 130°; the acid is moderately soluble in benzene or chloroform, and readily so in alcohol or ether. The barium salt [with $2H_2O$] crystallises from water in orange-red needles.

6-Nitro-*m*-tolylxyacetic acid [$O\cdot CH_2\cdot CO_2H : NO_2 : Me = 1 : 6 : 3$], prepared either by the action of ethyl chloroacetate on the corresponding nitro-*m*-cresol or by the nitration of *m*-tolylxyacetic acid, crystallises from aqueous alcohol in prismatic needles melting at 140–141° and dissolves slightly in water, moderately in benzene or chloroform, and readily in ether. T. H. P.

Syntheses with Sodamide. LUDWIG CLAISEN [and, in part, R. FEYERABEND, R. SCHULZE, and R. GÄRTNER] (*Ber.*, 1905, 38, 693–709).—Sodamide may be used profitably as a substitute for

sodium ethoxide in the condensation of ketones with esters; in many cases, the action occurs more readily and more rapidly than that of the ethoxide, and a better yield is obtained. This was found to hold in condensing ethyl acetate and ethyl benzoate with acetone and with acetophenone respectively, and in the preparation of hydroxy-methylene ketones. On the other hand, the use of sodamide does not give good results in the condensation of ketones with esters of nitrous acid, but the mono-alkylation of ketones is more readily effected by the action of sodamide on a cold ethereal solution of the ketone and alkyl iodide than by Nef's method; using this process, ethylacetophenone and benzylacetophenone can be readily obtained.

The action of sodamide on an ethereal solution of ethyl chloroacetate and acetophenone probably takes place in three stages, as follows:



Ethyl β-phenyl-β-methylglycidate, $\text{O} \begin{array}{c} \text{CPhMe} \\ \diagup \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$, is a colourless, somewhat viscid liquid which boils at 147—149° under 12 mm. and at 272—275° under the ordinary pressure; it has a sp. gr. 1.096 at 15°. The analogous *methyl* ester, $\text{C}_9\text{H}_9\text{O} \cdot \text{CO}_2\text{Me}$, prepared from methyl chloroacetate, has a sp. gr. 1.129 at 15°, and boils at 141—143° under 11 mm. and at 269—272° under the ordinary pressure. The *sodium salt*, $\text{O} \begin{array}{c} \text{CPhMe} \\ \diagup \end{array} \text{CH} \cdot \text{CO}_2\text{Na}$, obtained by mixing the ethyl ester

with sodium ethoxide dissolved in absolute alcohol and then adding water (1 mol.), forms white leaflets and melts and decomposes at 256°; the crystalline *barium* salt is rapidly decomposed by warm water and the *silver* salt is amorphous. The *amide*, $\text{C}_9\text{H}_9\text{O} \cdot \text{CO} \cdot \text{NH}_2$, crystallises from hot water in lustrous needles and melts at 168°; an isomeric *amide* is formed with it which crystallises from methyl alcohol in prisms or leaflets and melts at 151°.

When β-phenyl-β-methylglycidic acid is liberated from its sodium salt by adding acids, it at once decomposes, giving hydratrop-aldehyde (α-phenylpropaldehyde), $\text{CHPhMe} \cdot \text{CHO}$ (von Müller and Rohde, Abstr., 1891, 898), which boils at 203—205° and has a sp. gr. 1.012 at 15°; the *semicarbazone*, $\text{C}_{10}\text{H}_{13}\text{ON}_3$, crystallises from dilute alcohol in nacreous leaflets and melts at 153°; the *imino-derivative*, $\text{CPhMe} \cdot \text{CH} \cdot \text{NH}$, obtained by the direct action of aqueous ammonia on the aldehyde, separates from alcohol as a micro-crystalline powder and melts when rapidly heated at 114°. Ethyl β-phenyl-β-methylglycidate combines with hydrogen bromide to form *ethyl β-bromo-α-hydroxy-β-phenylbutyrate*, $\text{CPhMeBr} \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{Et}$, which crystallises in needles from light petroleum containing benzene and melts at 82—83°.

Ethyl β-phenyl-β-ethylglycidate, $\text{O} \begin{array}{c} \text{CPhEt} \\ \diagup \end{array} \text{CH} \cdot \text{CO}_2\text{Et}$, prepared from phenyl ethyl ketone and ethyl chloroacetate in presence of sodamide,

boils at 148—150° under 12 mm. pressure and has a sp. gr. 1.072 at 15°.

Ethyl ββ dimethylglycidate, $C_2H_{12}O_3$, prepared from acetone, boils at 180—182° and has a sp. gr. 1.016 at 15°; *sodium ββ-dimethylglycidate* crystallises in leaflets.

Ethyl β-methyl-β-ethylglycidate, $C_8H_{14}O_3$, obtained from methyl ethyl ketone, boils at 84—86° under 10 mm. and at 197—199° under the ordinary pressure; it has a sp. gr. 1.001 at 15°.

Ethyl β-methyl-β-propylglycidate boils at 91—92° under 11—12 mm. and at 211—212° under the ordinary pressure.

Ethyl ββ-diethylglycidate boils at nearly the same temperature as ethyl β-methyl-β-propylglycidate and has a sp. gr. 0.993 at 15°.

When benzaldehyde is condensed with ethyl chloroacetate under the influence of sodamide, ethyl β-phenylglycidate is the principal product, but some ethyl α-chlorocinnamate is also formed (compare E. Erlenmeyer, jun., Abstr., 1893, i, 36).
W. A. D.

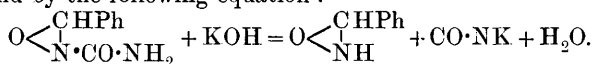
Nitro-derivatives of β-Resorcylic Acid [2:4-Dihydroxybenzoic Acid]. FRANZ VON HEMMELMAYR (*Monatsh.*, 1905, 26, 185—198. Compare Abstr., 1904, i, 319).—When heated with water at 160° in a sealed tube, nitro-β-resorcylic acid yields 4-nitroresorcinol, and must therefore be 5-nitro-2:4-dihydroxybenzoic acid.

The action of fuming nitric acid on nitro-β-resorcylic acid leads to the formation of 3:5-dinitro-2:4-dihydroxybenzoic acid, $C_7H_4O_8N_2$, which crystallises in clusters of flat, yellow needles, becomes colourless on exposure to the air, commences to sinter and to sublime at 180°, and melts at 205°. The *diammonium*, *potassium*, *dipotassium*, *barium*, $C_7H_2O_8N_2Ba \cdot 2H_2O$, and the *disilver* salts are described. When boiled with water in a reflux apparatus, the dinitro-acid loses carbon dioxide and yields 2:4-dinitroresorcinol, which melts at 147—148° (m. p. 145°, Lippmann and Fleissner, Abstr., 1886, 235, 791), and, when warmed with dilute nitric acid, yields styphnic acid. The barium derivative, $C_6H_2O_2(NO_2)_2Ba \cdot H_2O$, obtained by boiling 2:4-dinitroresorcinol with barium carbonate in aqueous solution, forms a reddish-yellow, crystalline, flocculent precipitate and loses H_2O at 130°; the barium derivative, $C_6H_2O_6N_2Ba \cdot 4H_2O$, formed by the action of barium chloride on the ammonium derivative of dinitroresorcinol, crystallises in microscopic, flat, yellow needles, loses $3H_2O$ at 130°, and H_2O at 180° (compare Bendikt, *Monatsh.*, 1881, 2, 324; Lippmann and Fleissner, *loc. cit.*).

In concentrated solution and with rapid cooling, styphnic acid forms a brownish-red, anhydrous, crystalline silver salt (compare Abstr., 1904, i, 814).
G. Y.

A New Reaction of Aldehydes, and the Isomerism of their Oximes. A. CONDUCHÉ (*Compt. rend.*, 1905, 140, 434—436).—Benzaldehyde condenses with isohydroxycarbamide (a molecular mixture of hydroxylamine hydrochloride and potassium cyanate, compare Francesconi and Parrozzani, Abstr., 1902, i, 139) to form a well-defined crystalline compound, $O \begin{smallmatrix} \text{CHPh} \\ \diagup \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$, melting at 125°, and similar compounds, produced from anisaldehyde, *m*-nitrobenzaldehyde,

furfuraldehyde, and heptaldehyde melting at 132° , 172° , 144° , and 85° respectively. The compound from salicylaldehyde decomposes at 100° . The compound from benzaldehyde is reduced by aluminium amalgam forming benzylcarbamide, and is decomposed by hydrochloric acid in aqueous solution, forming benzaldehyde and ammonium chloride, or in alcoholic solution yielding benzamide hydrochloride, ammonium chloride, and carbon dioxide. By the action of dilute aqueous or alcoholic potassium hydroxide, the benzaldehyde compound is converted into β -benzaldoxime and potassium cyanate, and in view of the fact that potassium cyanate condenses with β -benzaldoxime hydrochloride to give the benzaldehyde compound described above, whilst it does not react with the α -isomeride, the author maintains that the isomerism between the two benzaldoximes is structural and not spatial, and represents the formation of β -benzaldoxime from the benzaldehyde compound by the following equation :



M. A. W.

Additive Compounds of Hydrogen Bromide and Aromatic Carbonyl Compounds. THEODOR ZINCKE and G. MÜHLHAUSEN (*Ber.*, 1905, **38**, 753—760. Compare Abstr., 1903, i, 265; Vorländer, Abstr., 1903, i, 495; 1904, i, 65, 535, 900; Straus, Abstr., 1904, i, 899; Rosenheim and Levy, Abstr., 1904, i, 1024).—Diphenylbutadiene (diphenyldiethylene) and benzophenone do not form additive compounds with hydrogen bromide. When acted on by anhydrous hydrogen bromide, benzylideneacetone and dibenzylideneacetone are completely converted into resins, but in the presence of moisture the orange-red hydrobromides are formed.

p-Hydroxybenzaldehyde absorbs nearly 2 mols. of hydrogen bromide forming a white product. The action of hydrogen bromide on *p*-hydroxyacetophenone, in the solid state or dissolved in a mixture of chloroform and ether, leads to the formation of the colourless crystalline *hydrobromide*, $\text{C}_8\text{H}_8\text{O}_3 \cdot \text{HBr}$. *p*-Hydroxybenzophenone, with hydrogen bromide in ethereal solution, forms the yellow, crystalline *hydrobromide*, $\text{C}_{13}\text{H}_{10}\text{O}_3 \cdot \text{HBr}$, which yields *p*-hydroxybenzophenone when treated with water. In the solid state or in solution, *p*-hydroxybenzylideneacetone and *p*-dihydroxydibenzylideneacetone form coloured additive compounds with hydrogen bromide; these, when placed over potassium hydroxide, lose part of the hydrogen bromide, yielding the hydrobromides, $(\text{C}_{10}\text{H}_{10}\text{O}_2)_2 \cdot \text{HBr}$ and $\text{C}_{17}\text{H}_{14}\text{O}_3 \cdot \text{HBr}$. G. Y.

Benzophenonesulphone. FRITZ ULLMANN and ALFRED LEHNER (*Ber.*, 1905, **38**, 729—742. Compare Abstr., 1904, i, 417).—Tröger and Voigtländer-Tetzner (Abstr., 1897, i, 223), for the preparation of *o*-toluenesulphonic bromide, and Canter (Abstr., 1901, i, 208), for the preparation of phenyl-*o*-tolylsulphone, made use of commercial *o*-toluenesulphonic chloride containing 30 per cent. of the para-compound, and therefore obtained mixtures of ortho- and para-products.

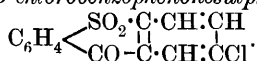
o-Toluenesulphonic chloride, prepared by the action of chlorine on potassium *o*-toluenesulphinate in aqueous solution, distils at 126°

under 10 mm. pressure and has a sp. gr. 1.3443 at 17°. *o*-Toluenesulphonic bromide, prepared by the action of bromine on *o*-toluenesulphinic acid in aqueous solution, melts at 13°, boils at 137.5—138° under 10 mm. pressure, and when shaken with aniline and aqueous sodium hydroxide forms *o*-toluenesulphanilide, $C_{13}H_{13}O_2NS$, which separates from benzene in small, colourless crystals and melts at 134°.

Phenyl-*o*-tolylsulphone, prepared by the action of aluminium chloride on *o*-toluenesulphonic chloride in benzene solution, forms small, glistening crystals, melts at 80°, and is oxidised by potassium permanganate in aqueous solution to diphenylsulphone-*o*-carboxylic acid, which melts at 144° (m. p. 152°; Graebe and Schultess, Abstr., 1891, 1058), and when heated in concentrated sulphuric acid at 180—190° yields benzophenonesulphone (Beckmann, *Ber.*, 1873, 6, 1112).

Phenyl-*p*-acetyl-amino-*o*-tolylsulphone, $NHAc \cdot C_6H_3Me \cdot SO_2Ph$, obtained by treating the amine (Norris, Abstr., 1901, i, 134) with acetic anhydride and glacial acetic acid, crystallises in colourless needles, melts at 183°, and when oxidised with potassium permanganate in aqueous solution yields 5-acetylaminodiphenylsulphone-2-carboxylic acid, $SO_2Ph \cdot C_6H_3(NHAc) \cdot CO_2H$, which forms yellow crystals and melts and decomposes at 212°.

4'-Chlorodiphenylsulphone-2-carboxylic acid, $C_6H_4Cl \cdot SO_2 \cdot C_6H_4 \cdot CO_2H$, is obtained as the potassium salt by heating potassium *o*-chlorobenzoate and *p*-chlorobenzenesulphinate with a trace of copper in aqueous solution at 135°; it crystallises in colourless leaflets. The acid crystallises in glistening, silky needles, melts at 151°, is easily soluble in alcohol, ether, or glacial acetic acid, and when heated with concentrated sulphuric acid at 195°, or when heated to 220—230° with phosphorus pentachloride, yields 3-chlorobenzophenonesulphone,



This crystallises in yellow needles, melts at 222°, and gives a blue coloration when warmed with zinc dust and sodium hydroxide in alcoholic solution.

2'-Methyldiphenylsulphone-2-carboxylic acid, $C_7H_7 \cdot SO_2 \cdot C_6H_4 \cdot CO_2H$, obtained by the condensation of potassium *o*-chlorobenzoate and *o*-toluenesulphinate in presence of copper, crystallises in large, colourless prisms, melts at 189°, is easily soluble in alcohol, glacial acetic acid, or boiling benzene, and when heated with concentrated sulphuric acid at 190° yields 5-methylbenzophenonesulphone, $C_{14}H_{10}O_3S$, which crystallises in leaflets, melts at 172°, and gives the characteristic blue coloration with zinc dust and sodium hydroxide in alcoholic solution.

4'-Methyldiphenylsulphone-2-carboxylic acid, obtained from *o*-chlorobenzoic and *p*-toluenesulphinic acids, melts at 155° and is soluble in alcohol, glacial acetic acid, boiling ether, or benzene. The methyl ester, $C_{15}H_{14}O_4S$, crystallises in colourless prisms and melts at 89°. 3-Methylbenzophenonesulphone, obtained by heating 4'-methyldiphenylsulphone-2-carboxylic acid in concentrated sulphuric acid, crystallises in yellow needles and melts at 199°.

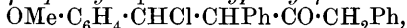
G. Y.

Formation of Salts of Benzoin. JAKOB MEISENHEIMER (*Ber.*, 1905, **38**, 874—878).—The sodium derivative of benzoin has not the formula $C_{42}H_{82}O_5Na_2$ attributed to it by Garner (this vol., i, 143), but when obtained pure, by carrying out the action between sodium and benzoin in an atmosphere of hydrogen, has the composition $C_{28}H_{23}O_4Na$. It is thus formed by the elimination of 1H from two mols. of benzoin, and is decomposed by water or acids quantitatively into the latter; in solution in presence of a slight excess of alkali, it is rapidly oxidised to benzoic acid and benzil, traces of benzilic acid being also formed.

Acetyl chloride converts it into benzoin and acetylbenzoin in molecular ratio, but alkyl iodides do not interact with it at all readily.

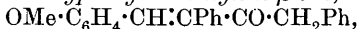
p-Nitrobenzoylbenzoin, $C_{21}H_{15}O_5N$, prepared from benzoin and *p*-nitrobenzoyl chloride, crystallises from benzene in yellow prisms, melts at 123° , and is converted by boiling sodium methoxide solution into benzil, several other substances having high melting points being also formed at the expense of the *p*-nitrobenzoic acid. W. A. D.

Condensation of Dibenzyl Ketone with Aldehydes under the Influence of Hydrochloric Acid. RICHARD HERTZKA (*Monatsh.*, 1905, **26**, 227—242. Compare Goldschmiedt and Knöpper, *Abstr.*, 1898, i, 31; 1899, i, 140).—*Chloro-p-methoxybenzyl*dibenzyl ketone (δ -chloro- $\alpha\gamma$ -diphenyl- δ -*p*-methoxyphenyl- β -butanone),



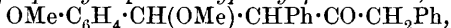
formed by the action of hydrogen chloride on a mixture of dibenzyl ketone and anisaldehyde cooled by ice, crystallises in rhombic plates, melts at 120 — 121° , and dissolves in concentrated sulphuric acid to a red solution, which, when diluted with water, yields a white flocculent precipitate.

$\alpha\gamma$ -Diphenyl- δ -*p*-methoxyphenyl- $\Delta\gamma$ -butylene- β -one,



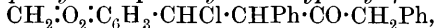
formed when *p*-methoxychlorobenzylidibenzyl ketone is heated at 140 — 160° under 12 mm. pressure or is treated with cold alcoholic potassium hydroxide, crystallises in white needles and melts at 98° .

δ -Methoxy- $\alpha\gamma$ -diphenyl- δ -*p*-methoxyphenyl- β -butanone,



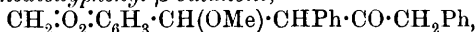
is formed when *p*-methoxychlorobenzylidibenzyl ketone is boiled with methyl alcohol; it crystallises in colourless, rhombic prisms, melts at 118 — 120° , and dissolves in concentrated sulphuric acid to a red solution. δ -Ethoxy- $\alpha\gamma$ -diphenyl- δ -*p*-methoxyphenyl- β -butanone, obtained in the same manner by the action of ethyl alcohol, crystallises in rhombic plates and melts at 92° .

δ -Chloro- $\alpha\gamma$ -diphenyl- δ -*m*-*p*-methylenedioxyphenyl- β -butanone,



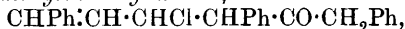
formed by the action of hydrogen chloride on a mixture of dibenzyl ketone and piperonal, is obtained as a white, crystalline mass, melts and decomposes at 106° , and dissolves in concentrated sulphuric acid to a brown solution, becoming violet on dilution. When heated at 130 — 150° under 12 mm. pressure, it yields $\alpha\gamma$ -diphenyl- δ -*m*-*p*-methylenedioxyphenyl- $\Delta\gamma$ -butene- β -one, $CH_2 \cdot O_2 \cdot C_6H_3 \cdot CH : CPh \cdot CO \cdot CH_2Ph$, which crystallises in yellow needles, melts at 120° , and dissolves in con-

concentrated sulphuric acid to a red solution. *δ*-Methoxy-*αγ*-diphenyl-*δ*-*m*-*p*-methylenedioxyphenyl-*β*-butanone,



obtained by boiling the chloro-compound in methyl alcohol, crystallises in needles and melts at 97°; the corresponding *ethoxy*-compound forms nodular crystals and melts at 87°.

α-Chlorocinnamenedibenzyl ketone,



formed by the condensation of dibenzyl ketone with cinnamaldehyde in presence of hydrogen chloride, melts at 107°. *n*-Chlorobutyldibenzyl ketone, obtained by the condensation of dibenzyl ketone with *n*-butaldehyde, forms white crystals and melts at 76°. G. Y.

Condensation of Phenylacetone with Phenanthraquinone.

HUGO LANG (*Monatsh.*, 1905, **26**, 199—215. Compare Japp and Klingemann, *Trans.*, 1891, **59**, 11; Goldschmiedt and Knöpper, *Abstr.*, 1898, i, 31; 1899, i, 140).—When warmed with piperidine or potassium hydroxide in alcoholic solution, phenylacetone and phenanthraquinone condense to phenanthroxylene-phenylacetone; if the condensation takes place in the presence of a small quantity of aqueous potassium hydroxide only, in addition to phenanthroxylene-phenylacetone, traces of an *isomeride*, which crystallises in yellow needles and melts at 196°, are formed.

Phenanthroxylene-phenylacetone, $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{C}=\text{CPh} \\ \text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{CH}_2 \end{matrix} > \text{CO}$, crystallises

in long, pale green needles, melts with slight decomposition at 188°, is easily soluble in chloroform, hot alcohol, ether, or benzene, but is insoluble in water, dilute acids, or aqueous alkali hydroxides, dissolves in concentrated sulphuric acid to an intensely bluish-green solution, and condenses with benzaldehyde in alcoholic potassium hydroxide solution to a *benzylidene* derivative, $\text{C}_{30}\text{H}_{20}\text{O}_2$, which crystallises in yellow needles and melts with slight decomposition at 234°.

The *phenylhydrazone*, $\text{C}_{20}\text{H}_{22}\text{ON}_2$, crystallises in long, reddish-brown needles and melts and decomposes at 181—184°; the *dibromide*, $\text{C}_{22}\text{H}_{16}\text{O}_2\text{Br}_2$, crystallises in rhombic plates, commences to decompose at 150°, and is completely melted at 175°. When boiled with zinc and hydrochloric acid in alcoholic solution, phenanthroxylene-phenylacetone is reduced to 1-phenyl-2:3-*o*-diphenylenecyclopentanone, $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHPh} \\ \text{C}_6\text{H}_4\cdot\text{CH}-\text{CH}_2 \end{matrix} > \text{CO}$, which crystallises in hexagonal plates, commences to decompose at 190°, melts at 233—236°, is easily soluble in hot benzene or chloroform, but only slightly so in water, alcohol, or ether, and dissolves in concentrated sulphuric acid to a yellowish-green solution; the *phenylhydrazone*, $\text{C}_{20}\text{H}_{24}\text{N}_2$, crystallises in brown needles and melts and decomposes at 220—222°.

When boiled with dilute sulphuric acid in a reflux apparatus, phenanthroxylene-phenylacetone is converted into isophenanthroxylene-phenylacetone, $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{CH}=\text{CH} \\ \text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{CHPh} \end{matrix} > \text{CO}$, which crystallises in slender, white prisms, melts with slight decomposition at 202°, is easily soluble

in benzene, carbon disulphide, or pyridine, and dissolves in concentrated sulphuric acid to a green solution; it decolorises alkaline potassium permanganate solution, and is reduced by zinc dust and hydrochloric acid in benzene solution to 1-phenyl-2:3-*o*-diphenylcyclopentanone. The *phenylhydrazone*, $C_{29}H_{22}ON_2$, crystallises in clusters of long, slender, red needles, commences to decompose at 150° , and melts at 191° ; the *dibromide*, $C_{23}H_{16}O_2Br_2$, crystallises in yellow leaflets and melts at 192° . G. Y.

Cinnamylidenecamphor and its Reduction Products. JULIUS W. BRÜHL (*Ber.*, 1905, **38**, 760—761).—A criticism of Rupe and Frisell's paper (this vol., i, 220). G. Y.

Gutta-percha-like Substance from the Resin of the Karite Tree. FRITZ FRANK and EDUARD MARCKWALD (*Chem. Centr.*, 1905, i, 186; from *Gummi Zeit.*, 1904, **19**, 167).—The resin of the Karite or Shea butter tree (*Bassia* or *Butyrospermum Parkii*) has the percentage composition gutta-percha 25.2, resin 57.13, plant constituents 5.76, mineral components 6.87, and water 5.04. The gutta substance, after purification, contains 8.31 per cent. of oxygen, and behaves like gutta-percha towards solvents. The nitrogen peroxide compound gave figures agreeing with those of Harries' nitrosite "c," $(C_{10}H_{16}O_7N_3)_2$.

The resin soluble in acetone is separated by extraction with acetone or alcohol into a resin of high melting point and a gummy resin. The resin has an odour of cinnamon, especially on boiling the less fusible fraction with potassium hydroxide, and probably yields cinnamic acid and lupeol. G. D. L.

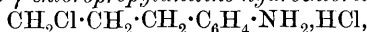
[Theory of Dyeing.] P. D. ZACHARIAS (*Ber.*, 1905, **38**, 816).—Polemical. A reply to Biltz (this vol., i, 224). A. McK.

Red Colouring Matter of Tomatoes. CARLO MONTANARI (*Chem. Centr.*, 1905, i, 544; from *Staz. sperim. agrar. ital.*, 1904, **37**, 909—919. Compare Arnaud, *Abstr.*, 1886, 712).—After removal of the seeds and skin and treatment with alcohol, the red colouring matter was extracted with carbon disulphide. After purification according to the method described by Arnaud, it crystallises from benzene in the form of deep red lamellæ and needles melting at 170° . On addition of iodine to the benzene solution, an amorphous, green precipitate of the composition $C_{52}H_{74}I_2$ separates. From this, it is concluded that the red colouring substance has the formula $C_{52}H_{74}$. Cryoscopic determinations of the molecular weight in benzene solution gave 635 and 650 (calculated for $C_{52}H_{74}$, 698). The substance is therefore not identical with carotene, $C_{26}H_{38}$, the colouring matter of carrots, but is to be regarded as a dicarotene. H. M. D.

Composition of Certain Invertebrate Pigments. ARTHUR B. GRIFFITHS (*Chem. News*, 1905, **91**, 90—91. Compare *Abstr.*, 1900, ii, 677; 1901, i, 94).—The red pigments of *Actinia mesembryanthemum* and of Ophiuroidea were isolated by treating the ethereal solutions with *N*/100 sodium hydroxide and evaporating in a vacuum.

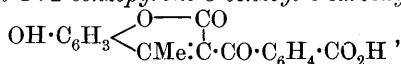
The actinia pigment has the composition $C_8H_9O_3N$ and in ethereal solution has $[\alpha]_D - 70.19^\circ$ at 18° . The Ophiuroidea pigment has the composition $C_{25}H_{24}O_3N_2$; it is soluble in ether, alcohol, chloroform, or benzene and when boiled with oxidising agents yields leucine and formic acid. The solution in ether has $[\alpha]_D - 97.84^\circ$ at 17° . The absorption spectra of both pigments are described and other red pigments from the animal kingdom are mentioned. D. A. L.

Synthesis of Chroman. JULIUS VON BRAUN and A. STEINDORFF (*Ber.*, 1905, 38, 850—855).—*o*- γ -Chloropropylbenzanilide (Abstr., 1904, i, 918), when treated with hydrochloric acid for 3—4 hours at 125 — 130° , gives *o*- γ -chloropropylaniline hydrochloride,



which crystallises in thick needles, melts and decomposes at 161° , and gives a corresponding *platinichloride* and *aurichloride*; on adding alkali to the hydrochloride, the base $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$ is first separated but this rapidly undergoes transformation into tetrahydroquinoline hydrochloride. *o*- γ -Chloropropylphenol, prepared from *o*- γ -chloropropylaniline sulphate by means of the diazo-reaction, boils at 150 — 151° under 13 mm. pressure, undergoing partial decomposition; with phenylcarbimide, it gives the *phenylcarbamate*, $C_{16}H_{16}O_2NCl$, which crystallises from light petroleum in globular aggregates of needles and melts at 74 — 76° . *Chroman*, $C_6H_4 \begin{smallmatrix} CH_2 \cdot CH_2 \\ \diagup \quad \diagdown \\ O \end{smallmatrix}$, prepared by warming an alkaline solution of *o*- γ -chloropropylphenol, boils at 214 — 215° under 749 mm. pressure and has an odour like peppermint. W. A. D.

Coumarin Derivatives from Ethyl *o*-Carboxy-phthalyl- and -benzyl-acetoacetates. CARL BÜLOW [with ERWIN SIEBERT] (*Ber.*, 1905, 38, 474—486. Compare Abstr., 1904, i, 609, 610).—7-Hydroxy-4-methyl-1:2-benzopyrone-3-*o*-phthalaldehydic acid [7-hydroxy-4-methyl-1:2-benzopyrone-3-benzoyl-*o*-carboxylic acid],



or the isomeric lactone obtained by the condensation of ethyl phthalyl-acetoacetate with resorcinol by means of dry hydrogen chloride in glacial acetic acid solution, crystallises from alcohol in colourless needles, melts at 180° , and is insoluble in water, ether, benzene, or light petroleum, and also in dilute sodium carbonate, yielding a yellow solution; this colour disappears to a large extent on the addition of a few drops of sodium hydroxide solution and subsequent heating at 50° . When fused for a few minutes with potassium hydroxide at 180 — 190° , the benzopyrone derivative yields resorcinol, resacetophenone, phthalic acid, and acetic acid. The formation of resacetophenone is made use of in supporting the constitutional formula already given.

The acetate, $OAc \cdot C_6H_3 \begin{smallmatrix} O-CO \\ \diagup \quad \diagdown \\ CMe : C \cdot CO \cdot C_6H_4 \cdot CO_2H \end{smallmatrix}$, melts at 152° and is insoluble in water, ether, or light petroleum and also in alkalis or alkali carbonate solutions.

A good yield of 5:7-dihydroxy-4-methyl-1:2-benzopyrone-3-*o*-phthalaldehydic acid [5:7-dihydroxy-4-methyl-1:2-benzopyrone-3-benzoyl-*o*-

carboxylic acid], $C_{18}H_{12}O_7$, is obtained from ethyl phthalylacetoacetate and phloroglucinol; it resembles the 7-hydroxy-derivative, and its solutions in dilute sodium carbonate have an orange-yellow colour. When dissolved in very dilute sodium hydroxide, the colour of the solution is first orange-yellow, but quickly changes to pale yellow. The isomeric 7:8-dihydroxy-derivative, obtained from pyrogallol, crystallises from alcohol or acetic acid and melts at 237° . Its solution in dilute sodium carbonate has a pure victoria-blue or light blue colour, which is almost completely removed by warming with sodium hydroxide, probably owing to its conversion into β -methylaphnetin- α -benzoyl-*o*-carboxylic acid.

Ethyl *o*-carboxybenzylacetoacetate also condenses with resorcinol yielding 7-hydroxy-4-methyl-1:2-benzopyrone-3-*o*-benzylcarboxylic acid, $OH \cdot C_6H_3 < \begin{smallmatrix} O- \\ CO \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CMe \\ C \end{smallmatrix} \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, which crystallises from alcohol in small, colourless needles melting at 283° , or from glacial acetic acid in hexagonal prisms. Its solutions in dilute alkalis have a blue fluorescence resembling that of Pechmann and Duisberg's β -methylumbelliferone. It is not precipitated from its alkaline solutions by means of carbon dioxide, and when boiled with 10 per cent. potassium hydroxide it yields resorcinol and benzylacetone-*o*-carboxylic acid (Abstr., 1887, 144); when fused with potassium hydroxide at 285 – 295° it yields resorcinol, resacetophenone, *o*-toluic acid, and acetic acid.

The *acetyl* derivative, $OAc \cdot C_6H_3 < \begin{smallmatrix} O- \\ CO \end{smallmatrix} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CMe \\ C \end{smallmatrix} \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, melts at 246 – 247° . The 5:7-dihydroxy- and 7:8-dihydroxy-compounds have both been prepared; the latter melts at 259 – 260° . J. J. S.

The Oxidising Action of Impure Ether. A. I. ROSSOLIMO (*Ber.*, 1905, 38, 774–775. Compare Decker, Abstr., 1903, i, 516; Berthelot, Abstr., 1881, 709).—When aqueous solutions of caffeine alkyl iodides are extracted with crude ether, a crystalline precipitate of a periodide is obtained. The formation is probably due to the oxidising action of a minute quantity of ethyl peroxide on the iodide, and it has been found that even a small amount of impure ether is capable of decomposing the whole of the caffeine alkyl iodide. The ether was a specimen of pure ether left in a wash-bottle for three months in contact with atmospheric oxygen. J. J. S.

Crystalline Alkaloid of Calycanthus Glaucus. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1905, 27, 144–155).—Calycanthine, the alkaloid obtained from the seeds, or rather achenes, of *Calycanthus glaucus*, was first described by Eccles (*Proc. Amer. Pharm. Assoc.*, 1888, 84, 382) and afterwards studied by Wiley (Abstr., 1890, 403).

After the oil has been extracted from the seeds, the residue contains about 2 per cent. of calycanthine. The alkaloid, $C_{11}H_{14}N_2 \cdot \frac{1}{2}H_2O$, crystallises in orthorhombic bipyramids and melts at 216 – 218° ; if heated for 3 or 4 hours at 120° , it becomes anhydrous and then melts at 243 – 244° . Calycanthine has a bitter taste, a slightly alkaline reaction towards litmus, and is very slightly soluble in water, but

readily so in ether or chloroform. The *hydrochloride*, *hydrobromide*, *hydriodide*, *sulphate*, *platinichloride*, *aurichloride*, *acetate*, and *picrate* are described. A list is given of various colour reactions which can be employed for the identification of the alkaloid.

Physiological experiments have shown that calycanthine produces symptoms similar to those brought about by strychnine. The alkaloid appears to act as a stimulant to the spinal cord and a depressant to the heart, and there is no doubt that it is the principal poisonous constituent of the seeds. E. G.

Constitution of α -iso- ψ -Cinchonine and of β -isoCinchonine. KARL KAAS (*Monatsh*, 1905, **26**, 119—125. Compare this vol., i, 151; Skraup and Zwerger, *Abstr.*, 1902, i, 305, 726).—When treated with methyl iodide in ethereal solution, α -iso- ψ -cinchonine forms the *hydriodide* of the methyl base, $C_{19}H_{21}ON_2Me, HI$, which decomposes at 248° , and when treated successively with ammonia and hydrochloric acid is converted into the *hydrochloride*. This is also obtained by heating α -isocinchonine methiodide with aqueous potassium hydroxide and treating the product with hydrochloric acid; it crystallises in rosettes of slender, white needles. α -iso- ψ -Cinchonine must be a keto-base, as its relation to α -isocinchonine is the same as that of cinchonine to cinchonine.

β -isoCinchonine dissolved in a mixture of chloroform and alcohol was treated with bromine, and, after one day, with ammonia; on extraction with ether and saturation of the ethereal solution with hydrogen chloride, the *hydrochloride* of the additive product with hydrogen bromide, $C_{19}H_{22}ON_2, HBr, 2HCl$, is obtained as a yellow precipitate. The treatment of α -iso- ψ -cinchonine with chlorine in concentrated hydrochloric acid solution leads in a similar manner to the formation of the *hydrochloride* of the additive compound with hydrogen chloride, $C_{19}H_{22}ON_2, HCl, 2HCl$, which is obtained as a yellow hygroscopic precipitate. α -iso- ψ -Cinchonine and β -isocinchonine therefore probably contain a vinyl group. G. Y.

Isomeric Coninium Iodides. II. MAX SCHOLTZ (*Ber.*, 1905, **38**, 595—600. Compare *Abstr.*, 1904, i, 1044).—The isomeric coninium iodides described in the first communication were prepared from coniine, which was purified by means of the hydrochloride and had $[\alpha]_D 14.8^\circ$. The coniine, used for the preparation of the salts now described, was purified by crystallisation of its hydrogen tartrate and had $[\alpha]_D +15.5^\circ$, a value in agreement with that of Ladenburg for the naturally occurring product. The action of benzyl iodide on 1-ethylconiine and on 1-isoamylconiine respectively was repeated, the latter specimen of coniine being used; the results previously obtained were confirmed.

α -Benzylethylconinium iodide, melting at 179° , is transformed at this temperature into the β -isomeride melting at 208° , the transformation apparently being complete. The reverse change does not take place. The physiological action of the two isomerides is also different, as also is that of the isomeric benzylpropyl-, benzylbutyl-, and benzylisoamylconinium iodides respectively.

1-Ethylconiine combines with allyl iodide to form a mixture of two isomeric coninium iodides, which are separated by fractional precipitation of the alcoholic solution of the mixture with ether.

α-Ethylallylconinium iodide, $C_8H_{16} \cdot N \cdot Et \cdot I \cdot C_3H_5$, is readily soluble in cold water, crystallises in microscopic prisms, and melts at 175° . *β-Ethylallylconinium iodide* is more sparingly soluble in water than the *α*-form, crystallises in needles, and melts at 191° .

Diallylconinium iodide, $C_{14}H_{26}NI$, prepared by the action of allyl iodide on coniine, separates from a mixture of alcohol and ether in leaflets and melts at 183° .

Dipropylconinium iodide, obtained as a by-product from the preparation of 1-propylconiine by interaction of coniine, propyl iodide, and potassium hydroxide, separates from a mixture of alcohol and ether in leaflets and melts at 219° .

The mixture of isomerides formed by the action of benzyl iodide on 1-propylconiine may be separated by water or by acetone, in either of which solvents the *α*-form is the more soluble. *α-Benzylpropylconinium iodide*, $C_{18}H_{30}NI$, separates from a mixture of alcohol and ether in needles and melts at 159° . *β-Benzylpropylconinium iodide* separates from water in microscopic prisms and melts at 196° .

1-Butylconiine, prepared from coniine, *n*-butyl iodide, and potassium hydroxide, boils at 223 — 224° (corr.) and has a sp. gr. 0.8393 at $20^\circ/4^\circ$ and $[\alpha]_D$ 72.6° . The separation of the isomerides formed by the action of benzyl iodide on 1-butylconiine is effected with some difficulty by means of acetone. *α-Benzylbutylconinium iodide*, $C_{19}H_{32}NI$, separates from water in needles and melts at 167 — 169° . *β-Benzylbutylconinium iodide* melts at 188° .

Crystallographic data respecting the isomeric benzylisoamylconinium iodides and the benzyethylconinium iodides are quoted.

A. McK.

Lysine. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1905, **43**, 363—364. Compare Abstr., 1891, 591).—*d*-Lysine platinichloride has the composition $C_6H_{14}O_2N_2 \cdot H_2PtCl_6 \cdot EtOH$, and *dl*-lysine platinichloride $C_6H_{14}O_2N_2 \cdot H_2PtCl_6$.

The preparation and analysis of the platinichlorides is recommended as a method for isolating lysine and also for distinguishing between *d*- and *dl*-lysine.

J. J. S.

[**Zirconichlorides of Organic Bases.**] ARTHUR ROSENHEIM and PAUL FRANK (*Ber.*, 1905, **38**, 812—816. See this vol., ii, 256).

Bromotetrahydroquinoline. FRANZ KUNCKELL and WILHELM THEOPOLD (*Ber.*, 1905, **38**, 848—850).—The *hydrobromide* of *bromoacetyltetrahydroquinoline* is obtained in well-formed, yellowish-red needles melting at 125° on brominating acetyltetrahydroquinoline in glacial acetic acid. *Bromoacetyltetrahydroquinoline*, $C_{11}H_{12}ONBr$, crystallises in colourless prisms melting at 60° and yields a *platinichloride* which crystallises in dark red, cubical plates and melts at 188° . *Bromotetrahydroquinoline*, prepared by the action of 20 per cent. hydrochloric acid on the foregoing acetyl derivative, separates in colourless crystals melting at 32 — 35° and forms a *hydrochloride*

melting at 198°. A monobromotetrahydroquinoline has been described by Königs (Abstr., 1883, 1143), which is perhaps identical with this.

E. F. A.

Transformation of Pyrrole into Indoles. Synthesis of 4:7-Dimethylindole. GIUSEPPE PLANCHER and A. CARAVAGGI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 157—161).—In order to establish the constitution of the base $C_{10}H_{11}N$, melting at 101—102° and obtained by condensing pyrrole with acetonylacetone by means of zinc acetate in acetic acid solution (see Plancher, Abstr., 1902, i, 640), as that of 4:7-dimethylindole, the authors have synthesised it from the *p*-xylylhydrazone of pyruvic acid. On condensing this compound in presence of zinc chloride, it yields 4:7-dimethylindole-2-carboxylic acid, $\begin{array}{c} \text{CH:CMc}\cdot\text{C-CH} \\ \text{CH:CMc}\cdot\text{C}\cdot\text{NH} \end{array} \gg \text{C}\cdot\text{CO}_2\text{H}$, which partially decomposes, giving 4:7-dimethylindole, $\begin{array}{c} \text{CH:CMc}\cdot\text{C-CH} \\ \text{CH:CMc}\cdot\text{C}\cdot\text{NH} \end{array} \gg \text{CH}$, melting at 101—102°.

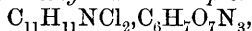
p-Xylylhydrazine, $C_8H_{12}N_2$, crystallises in colourless needles melting at 74° and undergoes rapid change when exposed to light and air. Its hydrochloride, $C_8H_{12}N_2\cdot\text{HCl}$, crystallises from water in shining, white scales melting at 206°.

Pyruvic acid *p*-xylylhydrazone, $C_{11}H_{14}O_2N_2$, forms a pale yellow precipitate which melts and decomposes at 164°. The ethyl derivative, $C_{13}H_{18}O_2N_2$, separates from aqueous alcohol in pale yellow crystals melting at 50°.

T. H. P.

Action of Chloroform on 2:3-Dimethylindole. Transformation of Pyrrole into Pyridine. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 162—165).—The authors find that the action of chloroform on 2:3-dimethylindole yields, besides 2:3-dimethyl-3-dichloromethylindolenine (compare Abstr., 1903, i, 449), another base which can be prepared from the latter, and which is shown to be 3-chloro-2:4-dimethylquinoline.

2:3-Dimethyl-3-dichloromethylindolenine picrate,



separates in reddish-yellow crystals melting at 164—165°. The oxime of the base, $C_{11}H_{10}ON_2Cl_2$, separates from benzene in crystals melting at 203°. The methiodide, $C_{12}H_{14}NCl_2I$, crystallises from alcohol in slender leaflets melting and decomposing at 220—221°.

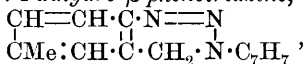
3-Chloro-2:4-dimethylquinoline, $C_{11}H_{10}NCl$, which can be obtained in larger quantity by heating 2:3-dimethyl-3-dichloromethylindolenine with sodium ethoxide at 100°, separates from aqueous alcohol in colourless, silky needles melting at 75°. The picrate, $C_{17}H_{13}O_7N_4Cl$, crystallises from alcohol in pale yellow prisms melting at 210°.

T. H. P.

Derivatives of *o*-Amino-*m*-xylyl-*p*-toluidine. REINHOLD VON WALTHER and R. BAMBERG (*J. pr. Chem.*, 1905, [ii], 71, 153—163. Compare Cohn and Fischer, Abstr., 1900, i, 690).—The following condensation products, $C_7H_7\cdot\text{NH}\cdot\text{CH}_2\cdot C_7H_6\cdot\text{N}\cdot\text{CHR}$, are formed by heat-

ing *o*-amino-*m*-xylyl-*p*-toluidine [6-amino-*m*-methylbenzyltoluidine] with the corresponding aldehydes.

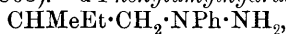
R = Me crystallises in slender, white needles and melts at 114°; R = Ph crystallises in white needles and melts at 125°; R = *o*-C₆H₄·NO₂ crystallises in sheaves of slender, orange needles and melts at 154·5°; R = *m*-C₆H₄·NO₂ crystallises in slender, yellow needles and melts at 132—133°; R = *p*-C₆H₄·NO₂ crystallises in long, orange needles and melts at 127—128°; R = *o*-C₆H₄·OH crystallises in slender, yellow needles and melts at 136—137°. The action of sodium nitrite on 6-amino-*m*-methylbenzyl-*p*-toluidine in glacial acetic acid solution or of amyl nitrite on the base in alcoholic solution leads to the formation of 3-*p*-tolyl-6-methyl-3 : 4-dihydro-β-phenotriazine,



which crystallises in slender, yellow needles, melts and decomposes at 173°, and is easily soluble in hot alcohol or benzene, but only slightly so in ether or light petroleum. With cold concentrated hydrochloric acid, it forms a yellow *hydrochloride*, which gradually dissolves in the acid; the *picrate*, C₂₁H₁₈O₇N₆, crystallises in nodules composed of orange, monoclinic prisms and melts and decomposes at 138°; the *platinichloride*, (C₁₅H₁₅N₃)₂·H₂PtCl₆, crystallises in yellow, hexagonal leaflets or in prismatic plates, becomes brown at 150°, and melts at 180°. When warmed with dilute acids, the phenotriazine evolves nitrogen and yields *o*-hydroxy-*m*-methylbenzyl-*p*-toluidine, C₇H₇·NH·CH₂·C₇H₆·OH, which dissolves in ether to a violet, fluorescent solution and forms a *picrate*, C₂₁H₂₀O₈N₄; this crystallises in small, transparent, yellow leaflets and melts and decomposes at 268·5°.

G. Y.

d-Phenylamylhydrazine. CARL NEUBERG and MAX FEDERER (*Ber.*, 1905, 38, 866—868).—*d*-Phenylamylhydrazine,



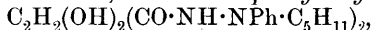
prepared by heating *d*-amyl bromide containing 94 per cent. of the pure substance with the sodium derivative of phenylhydrazine in presence of benzene, boils at 173—175° under 50 mm. pressure, and has a sp. gr. 0·9521; when distilled immediately after being prepared, it has $[\alpha]_D + 4^\circ 45'$, but on distilling after it has been kept for 6 weeks, it has $[\alpha]_D + 6^\circ 40'$. The *hydrochloride*, C₁₁H₁₈N₂·HCl, forms white crystals.

W. A. D.

Resolution of Racemic Substances. II. CARL NEUBERG and MAX FEDERER (*Ber.*, 1905, 38, 868. Compare *Abstr.*, 1903, i, 461).—*d*-Phenylamylhydrazine (preceding abstract) gives excellent results in resolving racemic ketones and aldehydes into their optically active forms. *l*-Arabinose-*d*-phenylamylhydrazone, C₁₀H₁₄O₆N₂, prepared from *l*-arabinose and the hydrazine, crystallises from a mixture of alcohol and water in nodular aggregates and melts at 127°. *d*-Arabinose-*d*-phenylamylhydrazone melts at 115° and is much more soluble than the *l*-form; on this account, *i*-arabinose is easily resolved into its constituents by combining it with *d*-phenylamylhydrazine.

d-Galactose-*d*-phenylamylhydrazone crystallises well from a mixture of alcohol and water and melts at 127—128°. *i*-Galactose is resolved almost quantitatively into its constituents by combining it with *d*-phenylamylhydrazine.

On heating racemic acid with *d*-phenylamylhydrazine and crystallising the product from water, *d*-tartaric-*d*-phenylamylhydrazide,



melting at 206°, is obtained; on hydrolysing it with aqueous barium hydroxide, *d*-tartaric acid is separated. 1-Tartaric-*d*-phenylamylhydrazide is easily soluble in water.

W. A. D.

Diquinolyls. STEFAN VON NIEMENTOWSKI and M. SEIFERT (*Ber.*, 1905, 38, 762—766. Compare Abstr., 1902, i, 21).—With either 2:2'-dinitrodiphenyl or arsenic acid as the oxidising agent, 2:2'-diaminodiphenyl undergoes Skraup's reaction, yielding 8:8'-diquinolyl, $\text{C}_{18}\text{H}_{12}\text{N}_2$; this crystallises in glistening, white leaflets or hexagonal plates, melts at 205—207°, is moderately soluble in hot alcohol, acetone, benzene, or carbon tetrachloride, easily so in chloroform, does not form a methiodide when heated with methyl iodide in methyl-alcoholic solution at 160° under pressure, and is nitrated only when heated with sulphuric and nitric acids at 180° in a sealed tube. The *hydrochloride*, $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot 2\text{HCl}$, forms stellate groups of crystals; the *hydrobromide*, $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot 2\text{HBr}$, obtained on heating the base with ethylene dibromide at 160°, forms microscopic, brown crystals; the *hydriodide*, $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot 2\text{HI}$, crystallises in leaflets and long spears and melts at about 250°; the *nitrate* crystallises in white, microscopic plates and melts and decomposes at 210—230°; the *sulphate*, $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot \text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$, forms white crystals; the *aurochloride*, $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot 2\text{HAuCl}_4$, crystallises in golden needles and melts and decomposes at 285°; the *platinichloride*, $\text{C}_{18}\text{H}_{12}\text{N}_2\cdot \text{H}_2\text{PtCl}_6$, is obtained as a yellow precipitate.

5:5'-Dimethyl-8:8'-diquinolyl, $\text{C}_{20}\text{H}_{16}\text{N}_2$, prepared by Skraup's reaction from 2:2'-diamino-4:4'-dimethyldiphenyl with arsenic acid as the oxidising agent, crystallises in yellow, tree-like aggregates of needles and leaflets, melts at 215°, is easily soluble in hot alcohol, acetone, chloroform, or benzene, and in its resistance to chemical reagents resembles diquinolyl. The *hydrochloride*, $\text{C}_{20}\text{H}_{16}\text{N}_2\cdot 2\text{HCl}$, crystallises in microscopic, white needles and melts and decomposes at about 320°; the *nitrate*, $\text{C}_{20}\text{H}_{16}\text{N}_2\cdot 2\text{HNO}_3$, crystallises in long, yellow spears and decomposes at 210°.

G. Y.

Influence of the Position of Methyl and Nitro-groups relatively to the Methane Carbon Atom on the Colours of Triphenylmethane Dyes. FRITZ REITZENSTEIN and OTTO RUNGE (*J. pr. Chem.*, 1905, [ii], 71, 57—132. Compare Abstr., 1904, i, 804; Nölting, Abstr., 1892, 187).—The introduction of methyl groups into hexa-alkyltriaminotriphenylmethane dyes in the meta-positions to the dialkylamino-groups is accompanied by a change in the colour from violet to blue, and finally to green, the colour changing with the increasing number of methyl-*m*-dialkylamino-groupings. The dark green colour of the 3:4':4''-hexamethyltriaminotriphenylmethane changes to a pure bluish-green in the dye of 3:4':4''-hexamethyltriamino-

6-methyltriphenylmethane, but, on the further introduction of methyl groups to form the tri-*o*-tolylmethane dye, the colour is merely weakened; this is due to the simultaneous presence of methyl-*m*-dialkylamino- and methyl-*p*-dialkylamino-systems, which neutralise each other.

The introduction of a nitro-group into the ortho-position of hexa-alkyltriaminotriphenylmethane dyes results in a change from dark to light green; if the nitro-group assumes the meta-position, the colour of the dye is weakened, whilst the reddish-blue of the 2:4':4''-hexamethyltriamino-5-methyltriphenylmethane dye becomes a pure blue in the *p*-nitro-derivative. This tendency to change from green to blue on introduction of a nitro-group is not displayed by the dyes derived from tetramethyldiaminoditolylhydrol.

The leuco-base, formed by condensation of tetramethyldiaminobenzhydrol and aniline in presence of hydrochloric acid, melts at 65° and consists of a mixture of *p*-amino- with a small quantity of *o* amino-leucomalachite-green; that obtained by condensation in presence of concentrated sulphuric acid melts at 60° and is a mixture of *o*-, *m*-, and *p*-aminoleucomalachite-greens (compare Nathanson and Müller, Abstr., 1889, 1188).

As has been shown by Nölting, the condensation of tetramethyldiaminobenzhydrols with aromatic bases leads to the formation of isomeric leuco-bases, the nature of the product depending on whether hydrochloric or sulphuric acid is used as the condensing agent; this also holds good for condensations with tetramethyldiaminoditolylhydrol.

Amongst others, the following new leuco-bases have been prepared by the condensation of tetramethyldiaminobenzhydrol with aromatic bases in presence of hydrochloric acid.

4-*Amino-4'*:4''-tetramethyldiamino-2-methyltriphenylmethane, from *m*-toluidine, is a blue powder, melts at 224—225°, and yields a blue dye. 4':4''-Tetramethyldiamino-2-ethylamino-5-methyltriphenylmethane, from ethyl-*p*-toluidine, is a white powder; the dye fixed with tartaric and tannic acids colours cotton-wool blue. 2:4':4''-Hexamethyltriamino-5-methyltriphenylmethane, from dimethyl-*p*-toluidine, is precipitated by ammonia as a white powder, which on filtration becomes a tar; the dye colours tannin mordanted cotton-wool blue.

4-*Amino-4'*:4''-tetramethyldiamino-2:3-dimethyltriphenylmethane, from *o*-xylylidine, forms nodular crystals and melts and decomposes at 168°; the dye colours tannin mordanted cotton-wool an intense blue.

The following leuco-bases, which have not been previously described, have been prepared by the condensation of tetramethyldiaminobenzhydrol with aromatic bases in presence of concentrated sulphuric acid.

3-*Methylamino-4'*:4''-tetramethyldiamino-4-methyltriphenylmethane, from methyl-*o*-toluidine, forms a light blue powder; the dye colours tannin mordanted cotton-wool green. 3-*Amino-4'*:4''-tetramethyldiamino-5-methyltriphenylmethane, from *m*-toluidine, is a blue powder; the dye colours tannin mordanted cotton-wool blue. 4':4''-Tetramethyldiamino-3-ethylamino-6-methyltriphenylmethane, from ethyl-*p*-toluidine, is a light blue powder; the dye colours tannin mordanted cotton-wool a bluish-green. 3:4':4''-Hexamethyltriamino-5-methyltriphenylmethane,

from dimethyl-*m*-toluidine, is obtained as a green, flocculent precipitate ; the dye colours tannin mordanted cotton-wool blue.

4' : 4''-Tetramethyldiamino-3-diethylamino-5-methyltriphenylmethane, from diethyl-*m*-toluidine, forms a brown powder and melts on the water-bath ; the zinc chloride salt of the dye forms glistening, bronze crystals and dyes cotton wool an intense blue.

In presence of hydrochloric acid, tetraethyldiaminobenzhydrol condenses with diethyl-*m*-toluidine to form 4 : 4' : 4''-hexaethyltri-amino-2-methyltriphenylmethane, which is brown ; the zinc chloride salt of the dye forms brown, glistening crystals and colours mordanted cotton-wool blue. The dye obtained on oxidation of the base formed by the condensation of tetraethyldiaminobenzhydrol and dimethyl-*m*-toluidine in presence of concentrated sulphuric acid forms a reddish-brown, crystalline double salt with zinc chloride and colours mordanted cotton-wool blue. The zinc chloride salt of the dye, obtained on oxidation of the condensation product of tetraethyldiaminobenzhydrol with diethyl-*p*-toluidine in presence of concentrated sulphuric acid forms glistening, bronze crystals and colours mordanted cotton-wool blue.

pp-Tetramethyldiaminodi-*o*-tolylmethane, $\text{CH}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_2)_2$, prepared by acting on dimethyl-*m*-toluidine with formaldehyde in alcoholic hydrochloric acid solution or in concentrated hydrochloric acid, crystallises in white, glistening leaflets, melts at 82° , and is converted into tetramethyldiaminodi-*o*-tolylhydrol by oxidation with lead peroxide in dilute acetic acid solution or electrolytically between lead electrodes in dilute sulphuric acid solution.

pp-Tetramethyldiaminodi-*o*-tolylhydrol, $\text{CH}(\text{C}_6\text{H}_3\text{Me}\cdot\text{NMe}_2)_2\cdot\text{OH}$, is also formed by electrolytic reduction of the corresponding ketone between lead electrodes in dilute sulphuric acid solution ; it is obtained as a white powder, which becomes brown on exposure to air and melts at about 50° . pp-Tetramethyldiaminodi-*o*-tolyl ketone is formed by the action of phosgene on dimethyl-*m*-toluidine at $100\text{--}150^\circ$; after removal of the excess of dimethyl-*m*-toluidine by a current of steam, the ketone is precipitated as the green, resinous substance on addition of sodium hydroxide.

Tetramethyldiaminoditolylhydrol condenses with aniline to form a mixture of leuco-bases ; in the presence of concentrated sulphuric acid, the product is a light blue powder, which on oxidation yields an earthy-blue dye ; the product, obtained in presence of hydrochloric acid, is a blue powder and yields a dull blue dye. With dimethylaniline in concentrated sulphuric acid, tetramethyldiaminoditolylhydrol forms a light brown powder, which melts at 85° , and on oxidation yields a dye, which dyes mordanted cotton-wool a dull blue.

The following leuco-bases were obtained by condensation of tetramethyldiaminoditolylhydrol with aromatic bases in presence of hydrochloric acid.

4-Amino-4' : 4''-tetramethyldiamino-3 : 2' : 2''-trimethyltriphenylmethane, from *o*-toluidine, is a light grey powder, yields a blue dye, and, on diazotisation, is converted into tetramethyldiaminotritolylmethane, which on oxidation yields a weak bluish-green dye.

2-Amino-4' : 4''-tetramethylamino-2' : 2'' : 5-trimethyltriphenylmethane,

from *p*-toluidine, sinters at about 62°, melts indefinitely at a higher temperature, and yields a greenish-blue dye. 4' : 4''-Tetramethyldiamino-2-ethylamino-2' : 2'' : 5-trimethyltriphenylmethane, from ethyl-*p*-toluidine, is obtained as a reddish-brown powder, which yields a bluish-green dye on oxidation. 4' : 4''-Hexamethyltriamino-2' : 2'' : 3-trimethyltriphenylmethane, from dimethyl-*o*-toluidine, crystallises from alcohol in white flakes, and, after oxidation, dyes mordanted cotton-wool a light blue. 2 : 4' : 4''-Hexamethyltriamino 2' : 2'' : 5-trimethyltriphenylmethane, from dimethyl-*p*-toluidine, becomes blue on oxidation. 4-Amino-4' : 4''-tetramethyldiamino-2 : 2' : 2'' : 3-tetramethyltriphenylmethane, from *o*-xylydine, crystallises from toluene and yields a bluish-green solution on oxidation. 2-Amino-4' : 4''-tetramethyldiamino-2' : 2'' : 3 : 5-tetramethyltriphenylmethane, from *m*-xylydine, is reddish-brown and becomes light green on oxidation. 4-Amino-4' : 4''-tetramethyldiamino-2 : 2' : 2'' : 5-tetramethyltriphenylmethane, from *p*-xylydine, separates from a mixture of benzene and petroleum in olive-green crystals and yields a green dye solution on oxidation.

The following leuco-bases were formed by the condensation of tetramethyldiaminoditolylhydrol with the aromatic bases named in concentrated sulphuric acid.

3-Amino-4' : 4''-tetramethyldiamino-2' : 2'' : 4-trimethyltriphenylmethane, from *o*-toluidine, melts at 120°, is oxidised to a weak bluish-green dye, and, on diazotisation, yields 4' : 4''-tetramethyldiamino-2' : 2'' : 3-trimethyltriphenylmethane, which is obtained as a yellow, granular powder. 3-Amino-4' : 4''-tetramethyldiamino-2' : 2'' : 5-trimethyltriphenylmethane, from *m*-toluidine, yields a weak blue dye solution. 5-Amino-4' : 4''-tetramethyldiamino-2 : 2' : 2''-trimethyltriphenylmethane, from *p*-toluidine, yields a green dye solution, and, on diazotisation, is converted into 4' : 4''-tetramethyldiamino-2 : 2' : 2''-trimethyltriphenylmethane, which is obtained as a yellow powder, becoming bluish-green on oxidation. 4' : 4''-Tetramethyldiamino-5-ethylamino-2 : 2' : 2''-trimethyltriphenylmethane, from ethyl-*p*-toluidine, is obtained as a grey precipitate, which becomes green on oxidation. 3 : 4' : 4''-Hexamethyltriamino-2' : 2'' : 4-trimethyltriphenylmethane, from dimethyl-*o*-toluidine, melts after sintering at 98°, and, when oxidised, dyes mordanted cotton-wool a weak green. 3 : 4' : 4''-Hexamethyltriamino-2' : 2'' : 5-trimethyltriphenylmethane, from dimethyl-*m*-toluidine, is obtained as a grey precipitate on addition of light petroleum to its solution in benzene, and forms a light blue solution when oxidised. 4' : 4'' : 5-Hexamethyltriamino-2 : 2' : 2''-trimethyltriphenylmethane, from dimethyl-*p*-toluidine, crystallises from a mixture of benzene and light petroleum, and, after oxidation, dyes tannin mordanted cotton a weak bluish-green. 3-Amino-4' : 4''-tetramethyldiamino-2' : 2'' : 4 : 5-tetramethyltriphenylmethane, from *o*-xylydine, separates from a mixture of benzene and light petroleum in grey crystals, and on oxidation yields a brown solution, which has no dyeing properties. 5-Amino-4' : 4''-tetramethyldiamino-2 : 2' : 2'' : 4-tetramethyltriphenylmethane, from *m*-xylydine, separates from a mixture of toluene and light petroleum in grey crystals, and, on oxidation, yields a weak brown dye. 3-Amino-4' : 4''-tetramethyldiamino-2 : 2' : 2'' : 5-tetramethyltriphenylmethane, from *p*-xylydine, is light blue, and on oxidation yields a brown solution.

In hydrochloric acid, tetramethyldiaminobenzhydrol condenses with *o*-nitro-*p*-toluidine to form 4-nitro-2-amino-4':4''-tetramethyldiamino-5-methyltriphenylmethane, which is obtained as a resin, and, when oxidised, dyes tannin mordanted cotton-wool an intense blue. In concentrated sulphuric acid, the condensation leads to the formation of 5-nitro-3-amino-4':4''-tetramethyldiamino-6-methyltriphenylmethane, which is obtained as a green substance; the dye solution colours mordanted cotton-wool a light bluish-green. In hydrochloric acid, the hydrol condenses with *p*-nitro-*o*-toluidine to form 5-nitro-2-amino-4':4''-tetramethyldiamino-3-methyltriphenylmethane, which is obtained as a green powder, and, after oxidation, colours mordanted cotton-wool a dark blue. In concentrated sulphuric acid, the condensation with *p*-nitro-*o*-toluidine leads to the formation of 6-nitro-3-amino-4':4''-tetramethyldiamino-4-methyltriphenylmethane, which, after oxidation, dyes tannin mordanted cotton-wool a light bluish-green. With *o*-nitrodimethyl-*p*-toluidine in hydrochloric acid, the benzhydrol condenses to 4-nitro-2:4':4''-hexamethyltriamino-5-methyltriphenylmethane, which is obtained as a resin; the dye colours tannin mordanted cotton-wool an intense blue. In concentrated sulphuric acid, this condensation leads to the formation of 5-nitro-3:4':4''-hexamethyltriamino-6-methyltriphenylmethane, which is obtained as a resin; the dye solution colours tannin mordanted cotton-wool green. In hydrochloric acid, the benzhydrol condenses with *p*-nitrodimethyl-*o*-toluidine to form 5-nitro-2:4':4''-hexamethyltriamino-3-methyltriphenylmethane, which, after oxidation, dyes mordanted cotton-wool an intense blue. In concentrated sulphuric acid, this condensation leads to the formation of 6-nitro-3:4':4''-hexamethyltriamino-4-methyltriphenylmethane, which, after oxidation, dyes tannin mordanted cotton-wool a light green.

Tetramethyldiaminoditolyhydrol condenses slowly with *o*-nitro-*p*-toluidine to form 5-nitro-3-amino-4':4''-tetramethyldiamino-2':2'':6-trimethyltriphenylmethane; the yellowish-brown leuco-base, on oxidation, yields a brown solution. 4-Nitro-2-amino-4':4''-tetramethyldiamino-2':2'':5-trimethyltriphenylmethane, obtained by this condensation in hydrochloric acid, is an olive-green substance, which, on oxidation, yields a bluish-green dye solution. With *p*-nitro-*o*-toluidine in concentrated sulphuric acid, the ditolyhydrol condenses to 6-nitro-3-amino-4':4''-tetramethyldiamino-2':2'':4-trimethyltriphenylmethane; the yellowish-brown leuco-base, on oxidation, yields a brown solution. 6-Nitro-4-amino-4':4''-tetramethyldiamino-2':2'':3-trimethyltriphenylmethane, formed by the condensation with *p*-nitro-*o*-toluidine in hydrochloric acid, is an olive-green substance, which, on oxidation, yields a bluish-green dye solution.

When boiled with 1-chloro-2:4-dinitrobenzene and sodium acetate in absolute alcoholic solution in a reflux apparatus, the leuco-base obtained by condensation of tetramethyldiaminobenzhydrol and aniline in presence of concentrated sulphuric acid yields a dinitroanilino-leuco-base, which is a dark red powder and melts at about 154°; an orange-coloured substance melting at 171° crystallises slowly from the alcoholic mother liquor. A similar reddish-brown dinitroanilino-leuco-base is obtained from the hydrochloric acid condensation product of tetramethyldiaminobenzhydrol and aniline; these leuco-bases, when dis-

solved in hydrochloric acid, colour tannin mordanted cotton-wool yellow, and gelatinise when oxidised with lead peroxide. The *dinitroanilino-leuco-base*, obtained from the sulphuric acid condensation product of tetramethyldiaminoditolyhydrol and aniline, is a brownish-red substance, which, after oxidation, dyes tannin mordanted cotton-wool a weak earthy-green. The dye solution, obtained in the same manner from the hydrochloric acid condensation product of the ditolyhydrol and aniline, is a weak blue.

The following dinitroanilino-leuco-bases are prepared in the same manner from the corresponding leuco-bases.

o-Dinitroanilinoleucomalachite-green, is a yellow substance which in hydrochloric acid solution dyes tannin mordanted cotton-wool yellow and gelatinises on oxidation. *3-Dinitroanilinoleucomalachite-green* is a cochineal-coloured substance, which dyes tannin mordanted cotton-wool yellow in hydrochloric acid solution and yields a *dye*, which forms glistening, red crystals and colours tannin mordanted cotton-wool a yellowish-green. *4-Dinitroanilinoleucomalachite green* is a yellowish-brown substance, which dyes tannin mordanted cotton-wool a weak sulphur-yellow, and gelatinises when oxidised. *4' : 4''-Tetramethyldiamino-3-dinitroanilino-4-methyltriphenylmethane* is a reddish-brown substance, which, when oxidised, yields a green dye. *4' : 4''-Tetramethyldiamino-3-dinitroanilino-5-methyltriphenylmethane* is a yellowish-brown substance, melts at 200—201°, dyes tannin mordanted cotton-wool a lemon-yellow in hydrochloric acid solution, and is oxidised by lead peroxide to an intense earthy-green; when reduced with zinc dust in dilute hydrochloric acid solution, the leuco-base yields a brown *product*, which, when oxidised, dyes tannin mordanted cotton-wool steel-blue. *4' : 4''-Tetramethyldiamino-3-dinitroanilino-6-methyltriphenylmethane* is a dark red substance, which, when oxidised, yields an intense green dye and is reduced by zinc dust in hydrochloric acid solution to the aminonitrophenyl derivative; this brown leuco-base yields on oxidation an intense bluish-green dye. *4' : 4''-Tetramethyldiamino-3-dinitrophenylethylamino-6-methyltriphenylmethane* is a reddish-brown substance, which yields an intense green dye. *4' : 4''-Tetramethyldiamino-4-dinitroanilino-2-methyltriphenylmethane* is reddish-brown, melts at 197°, and is oxidised to an intense earthy-green dye. *4' : 4''-Tetramethyldiamino-2-dinitroanilino-2' : 2''-dimethyltriphenylmethane* is reddish-brown and yields a dye solution, which colours tannin mordanted cotton-wool a dirty green. *4' : 4''-Tetramethyldiamino-3-dinitroanilino-2' : 2''-dimethyltriphenylmethane* is reddish-brown and yields, on oxidation, a weak green dye solution. *4' : 4''-Tetramethyldiamino-4-dinitroanilino-2' : 2''-dimethyltriphenylmethane* is a brown powder; the dye solution is a dull green. *4' : 4''-Tetramethyldiamino-3-dinitroanilino-2' : 2''-6-trimethyltriphenylmethane* is yellow, and on oxidation yields a dye solution which colours tannin mordanted cotton-wool yellowish-green.

The acetyl and *p*-toluenesulphonyl derivatives of *m*-aminoleuco-bases were found to yield green dye solutions. G. Y.

New Reaction of Semicarbazones. III. Preparation of the Hydrazides of Aromatic Substituted Carbamic Acids from Semicarbazide. WALTHER BORSCHÉ (*Ber.*, 1905, 38, 831—837. Compare Abstr., 1902, i, 186).—Phenylcarbamic hydrazide hydro-

chloride and similar compounds are conveniently prepared by heating acetone or acetophenone semicarbazone with aniline and subsequently decomposing the hydrazone formed by heating with hydrochloric acid. *Ethyl acetophenonecarboxylatehydrazone* crystallises in colourless needles which melt at 119—120°; on heating with aniline, it forms *acetophenonephenylcarbamic acid hydrazone*, melting at 187—188°, and crystallises in colourless needles. *p-Tolylcarbamic hydrazide* crystallises in colourless plates melting at 259—260°, the *hydrochloride* forms colourless, silky, glistening needles melting at 242°. It yields hydrazone derivatives with aldehydes and ketones; *acetone-p-tolylcarbamic hydrazone*, $\text{CMe}_2\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, separates in needles aggregated in clusters and melts at 174—175°; the corresponding *acetophenone* compound, $\text{CMePh}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, melts at 192° and the *o*-hydroxybenzylidene-*p*-tolylcarbamic hydrazone,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$,
at 238—239°. *p-Hydroxybenzeneazoformo-p-toluidide*,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$,
forms small, red crystals melting at 173—174°.

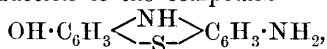
o-Tolylcarbamic hydrazide melts at 142—143°; the *hydrochloride* separates in silvery, glistening needles and plates or in colourless cubes and melts at 184—186°; the acetonehydrazone melts at 156°, the acetophenonehydrazone at 211—212°, and the *o*-hydroxybenzylidene derivative at 204·5°, whilst the dark red crystals of *o-hydroxybenzeneazoformo-o-toluidide* melt at 164—165°.

β-Naphthylcarbamic hydrazide forms a colourless powder melting at 258—259°; the *hydrochloride* decomposes at 230° and is completely melted at 260°. The *acetophenone* derivative melts at 201—202°, the *o-hydroxybenzylidene* derivative at 251—252°, and *p-hydroxybenzeneazoformo-β-naphthylamide* at 189—190°.

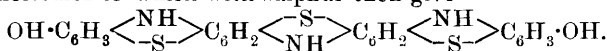
E. F. A.

The Presence and Action of Mercaptan Groups in Direct Sulphur Dyes. RAYMOND VIDAL (*Chem. Centr.*, 1905, i, 411—412; from *Mon. scient.*, [iv], 19, i, 25).—The solubility of the sulphur dyes in alkali sulphides is not necessarily due to mercaptan groups, but may result from the presence of phenolic groups.

When *p*-aminophenol is melted with sulphur in sufficient quantity to form the thiazine, a bluish-black dye soluble in cold sodium sulphide is formed. When heated with sodium sulphide, a blue or bluish-black colour assumes a greenish shade the more readily when few substituents are present, that is, when the chances of the introduction of mercaptan groups, to which the colour change is due, are greatest. Substituents do not exercise so great an influence on the shade as the proportions of materials and the temperature used in the preparation. The author explains the formation of Vidal-black from *p*-aminophenol and sulphur by the production of the compound

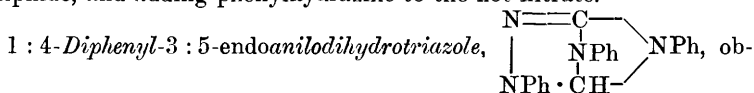


two molecules of which with sulphur then give



G. D. L.

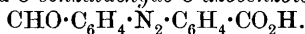
endoIminotriazoles. MAX BUSCH (*Ber.*, 1905, **38**, 856—860).—Trialkylaminoguanidines of the type $\text{NHR}'\cdot\text{C}(\text{NHR}'')\cdot\text{N}\cdot\text{NHR}$ are readily prepared by the interaction of carbodiphenylimides with alkylhydrazines; this method of preparation was attempted by Wessel (*Abstr.*, 1888, 1083), but without success owing to the action having been allowed to go too far. Triphenylaminoguanidine, $\text{C}(\text{NHPh})_2\cdot\text{N}\cdot\text{NHPH}$, is prepared by heating thiocarbamilide with mercuric oxide and benzene, removing the precipitated mercuric sulphide, and adding phenylhydrazine to the hot filtrate.



tained by heating triphenylaminoguanidine with formic acid at 175° , crystallises from alcohol in highly lustrous, yellow leaflets or plates and melts and decomposes at 189° ; it resists the action of acids, but is easily hydrolysed by alcoholic potassium hydroxide initially into its constituents, the triphenylaminoguanidine then being oxidised to benzene-azoanilinophenyliminomethane, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{NHPh})\cdot\text{NPh}$. *Diphenylendoanilodihydrotriazole nitrate*, $\text{C}_{20}\text{H}_{16}\text{N}_4\cdot\text{HNO}_3$, is extraordinarily sparingly soluble in water (compare this vol., ii, 283); the *sulphate*, $\text{C}_{20}\text{H}_{16}\text{N}_4\cdot\text{H}_2\text{SO}_4$, melts at $100\text{--}101^\circ$, and the *hydrochloride* at 242° . Formic acid gives rise to two *salts*: (1) $\text{C}_{20}\text{H}_{16}\text{N}_4\cdot\text{CH}_2\text{O}_2$ melts and decomposes at 168° ; (2) $\text{C}_{20}\text{H}_{16}\text{N}_4\cdot 2\text{CH}_2\text{O}_2$ forms large, lustrous needles and melts and decomposes at 128° . The following salts also form good crystals: the *hydriodide*, *perchlorate*, *bromate*, *sulphite*, and *cyanate*.

W. A. D.

Decomposition of *o*-Nitrobenzyl Alcohol under the Influence of Aqueous and of Alcoholic Sodium Hydroxide. PAUL CARRÉ (*Compt. rend.*, 1905, **140**, 663—665. Compare Freundler, *Abstr.*, 1904, i, 667).—When *o*-nitrobenzyl alcohol is warmed with aqueous sodium hydroxide, the chief products are anthranilic acid, *o*-azobenzoic acid, and *o*-benzaldehyde-*o*-azobenzoic acid,



The aldehyde acid was not isolated, but its *oxime*, which crystallises from acetic acid in orange spangles melting at 232° , and its *semi-carbazone*, which forms orange needles melting at 240° , were obtained. The aldehyde acid changes, slowly in the cold, rapidly on warming, into a pale yellow compound melting at 294° , which is represented by the formula $(\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2)_2$.

In smaller quantities, *o*-nitrobenzaldehyde and *o*-aminobenzaldehyde are produced. The former gives a *p*-nitrophenylhydrazone in the form of small, red prisms which melt at 263° . The chloride of the latter gives a double chloride with mercury of the formula



this crystallises from water in needle-shaped crystals melting at 149° .

There were no indications of the formation of azoxybenzoic acid or of nitrotoluene, which is contrary to the statements of Jaffé (*Zeit. physiol. Chem.*, 1878, **2**, 55).

When acted on by alcoholic soda, the principal products are *o*-indazyl-

benzoic acid and benzaldehyde *o*-azobenzoic acid. In smaller quantities, *o*-aminobenzyl alcohol, *o*-indazylbenzyl alcohol, *o*-aminobenzaldehyde, anthranil, and anthranilic acid are obtained. Sodium ethoxide acts on the *o*-nitrobenzyl alcohol in a similar manner, but the proportion of the alcohol group which is unaltered is greater in this case. H. M. D.

Action of Cuprous Chloride on Aryldiazonium Salts. FRITZ ULLMANN and L. FRENTZEL (*Ber.*, 1905, 38, 725—729. Compare Abstr., 1902, i, 89).—The action of cuprous chloride on *m*-nitrobenzene-diazonium sulphate leads to the formation of a small quantity of *m*-chloronitrobenzene together with a much larger quantity of 3 : 3'-dinitrodiphenyl (87 per cent.). In the same manner, about equal quantities of *p*-chloronitrobenzene and 4 : 4'-dinitrodiphenyl were obtained from *p*-nitroaniline.

The following new substances were obtained by this method :

2 : 2'-Dinitrodiphenyl-4 : 4'-disulphonic acid is obtained as a brown mass from diazotised 2-nitroaniline-4-sulphonic acid ; the potassium salt, $C_{12}H_6O_{10}N_2S_2K_2$, crystallises in yellow leaflets. 3 : 3'-Dinitro-4 : 4'-ditolyl, $C_{14}H_{12}O_4N_2$, obtained along with *p*-chloro-*o*-nitrotoluene from *o*-nitro-*p*-toluidine, separates from glacial acetic acid in brown crystals, melts at 175·5°, and is easily soluble in boiling benzene. 6 : 6'-Dinitro-2 : 2'-ditolyl, obtained along with *o*-chloro-*m*-nitrotoluene from *m*-nitro-*o*-toluidine or by heating *o*-chloro-*m*-nitrotoluene with copper powder, crystallises in small, yellow needles, melts at 110°, and is easily soluble in alcohol or benzene. 5 : 5'-Dinitro-2 : 2'-ditolyl, obtained along with 5 : 5'-dinitro-2 : 2'-azotoluene and *o*-chloro-*p*-nitrotoluene from *p*-nitro-*o*-toluidine, crystallises in yellow needles, melts at 173°, and is easily soluble in glacial acetic acid or benzene. 5 : 5'-Dinitro-2 : 2'-azotoluene, $C_{14}H_{12}O_4N_4$, crystallises in red needles, melts at 273°, and is only slightly soluble in boiling alcohol, benzene, or toluene. 4 : 4'-Dinitro-2 : 2'-ditolyl, obtained along with 2-chloro-5-nitrotoluene and 4 : 4'-dinitro-2 : 2'-azotoluene from 5-nitro-2-toluidine, crystallises in yellow leaflets, melts at 170°, and is easily soluble in boiling benzene or glacial acetic acid.

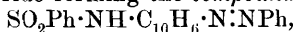
4 : 4'-Dinitro-2 : 2'-azotoluene crystallises in reddish-brown leaflets, melts at 258°, and is easily soluble in benzene, glacial acetic acid, or nitrobenzene. G. Y.

***o*-Aminoazo-dyes.** MAX BUSCH and ED. BERGMANN (*Zeit. Farb. Text. Ind.*, 1905, 4, 105—113).—The following experiments show that *o*-aminoazo-derivatives have a normal constitution, but that they readily undergo transformation into the isodynamic form, $NH:C_6H_4:N:NHR$, becoming thus susceptible to the so-called ortho-transformations.

o-Aminoazo-*p*-toluene readily condenses with benzenesulphonic chloride dissolved in benzene solution containing pyridine to form benzenesulphonamino-*o*-azo-*p*-toluene, $SO_2Ph \cdot NH \cdot C_6H_3Me \cdot N:N \cdot C_6H_4Me$, which crystallises from alcohol in yellow needles and melts at 155° ; it does not dissolve in aqueous alkalis, but with alcoholic sodium hydroxide gives rise to a sodium derivative which remains dissolved

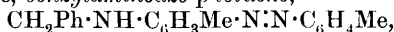
on diluting with water. The analogous benzenesulphonamino-*p*-azotoluene, on the other hand, is soluble in aqueous sodium hydroxide.

o-Benzeneazo- β -naphthylamine combines in similar manner with benzenesulphonic chloride forming the compound



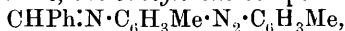
which crystallises from alcohol in slender, red needles and melts at 167°.

On heating *o*-aminoazo-*p*-toluene with benzyl chloride and alcoholic sodium hydroxide, *benzylaminoazo-p-toluene*,

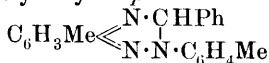


is obtained; it crystallises from a mixture of alcohol and ether in bright red needles or prisms, melts at 75°, gives a brownish-yellow crystalline *hydrochloride*, and combines with sodium nitrite, giving the *nitrosoamine*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$, which crystallises from alcohol in yellow needles melting at 116°.

On oxidising *benzylaminoazo-p-toluene* in acetone solution with potassium permanganate, the *benzylidene* compound,



is obtained; on warming this with glacial acetic acid, it is transformed into phenyl-*p*-tolylldihydro-*p*-tolutriazine,

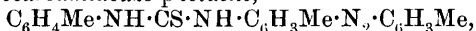


(Goldschmidt and Rosell, Abstr., 1890, 614), which melts at 227° instead of 220° as formerly stated.

p-Aminoazobenzene combines with phenylthiocarbimide to form *p*-phenylthiocarbamidoazobenzene, $\text{N}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, which differs from the analogous derivative formed from *o*-aminoazobenzene by not losing hydrogen sulphide when treated with mercuric oxide; it is converted instead into *p*-phenylthiocarbamidoazobenzene.

o-Aminoazotoluene and methylthiocarbimide give *methylthiocarbamidoazotoluene*, $\text{NHMe}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me}$, which crystallises from alcohol in thick needles and melts at 154–155°; it differs from the corresponding derivative prepared from phenylthiocarbimide by not being changed by boiling glacial acetic acid, and mercuric oxide in benzene fails also to convert it into a triazine derivative.

2-o-Tolylthiocarbamidoazo-p-toluene,



prepared from *o*-aminoazo-*p*-toluene and *o*-tolylthiocarbimide, crystallises from alcohol in brownish-yellow leaflets, melts at 157°, and is easily transformed by glacial acetic acid into *o-tolylimino-p-tolyl-p-tolutriazine*, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{N}\cdot\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me(o)} \\ \text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me(p)} \end{array}$, which crystallises from a

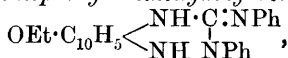
mixture of ether and light petroleum in bluish-black needles and melts at 167°.

2-m-Nitrophenylthiocarbamidoazo-p-toluene, prepared from *o*-aminoazotoluene and *m*-nitrophenylthiocarbimide, forms yellowish-brown leaflets, melts at 164°, and is converted by mercuric oxide into *m-nitrophenyliminotolyltolutriazine*, $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{N}\cdot\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \\ \text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me} \end{array}$, which forms dark grey, felted needles and decomposes at about 185–190°.

Phenylazo- β -naphthylamine does not give a thiocarbamido-derivative with phenylthiocarbimide, but on heating the two substances with benzene and mercuric oxide, *phenyliminophenyl-naphthatriazine*, $C_{10}H_6 \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{C} \cdot \text{NPh} \end{smallmatrix}$, is obtained; it crystallises from alcohol in bluish-black needles, and from a mixture of benzene or light petroleum in thick, brownish-yellow, transparent leaflets, melts at 166° , and gives a *hydrochloride*, $C_{23}H_{16}N_4 \cdot HCl$, crystallising in bright red aggregates and melting at 248° ; the *nitrate* is very sparingly soluble in water.

2-Benzeneazo-4-bromo-1-naphthylamine, $NH_2 \cdot C_{10}H_5Br \cdot N_2Ph$, obtained from 4-bromo-1-naphthylamine and benzenediazonium chloride, crystallises from alcohol in brownish-red needles and melts at 146° ; the *hydrochloride* melts at 195° . In alcoholic solutions, the azo-compound combines slowly with phenylcarbimide, forming *phenyliminophenyl-bromonaphthatriazine*, $C_{10}H_5Br \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{NPh} \\ \text{N} \cdot \text{NPh} \end{smallmatrix}$, which crystallises from alcohol in lustrous, blue needles, melts at 189° , and gives a yellow, crystalline *hydrochloride*.

Benzeneazo-4-ethoxy-1-naphthylamine, prepared from 1-amino-4-ethoxynaphthalene, crystallises from alcohol in red, silky needles, melts at 142° , and combines readily with phenylthiocarbimide to form *phenyliminophenyl-4-ethoxynaphthatriazine*, $OEt \cdot C_{10}H_5 \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{NPh} \\ \text{N} \cdot \text{NPh} \end{smallmatrix}$, which separates from xylene in lustrous, blue crystals and melts at 230° ; the *hydrochloride*, $C_{25}H_{20}ON_4 \cdot 1\frac{1}{2}HCl$, is abnormal, and the *picrate* melts at 195° . On reduction with hydrogen sulphide, the triazine gives *phenyliminophenyl-4-ethoxydihydronaphthatriazine*,



which crystallises from alcohol in colourless, lustrous needles and melts at 207° .

The *triazine*, $OEt \cdot C_{10}H_5 \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{NPh} \\ \text{N} \cdot \text{N} \cdot \text{C}_{10}H_5 \cdot OEt \end{smallmatrix}$, prepared from the azo-compound, (4) $OEt \cdot C_{10}H_5(NH_2) \cdot N_2 \cdot C_{10}H_5 \cdot OEt$ (1:4), obtained from 1-amino-4-ethoxynaphthalene, crystallises in violet needles and melts at 275° ; the salts are bright red.

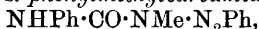
Phenylethoxyketonaphthatriazine, $C_6H_4 \begin{smallmatrix} \text{C} \cdot \text{N} \cdot \text{CO} \\ \text{C}(OEt) \cdot \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{NPh} \end{smallmatrix}$, prepared by the action of carbonyl chloride on benzeneazoaminoethoxynaphthalene in benzene solution, crystallises from alcohol in yellow needles and melts at 236° .

Diazoamino-p-anisole, $OMe \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4 \cdot OMe$, prepared from *p*-anisidine, crystallises from a mixture of ether and light petroleum in yellowish-brown prisms and melts at 101.5° ; on attempting to convert it into *o*-aminoazoanisole, it gives rise to the *azophenine*, $C_6H_2(NH \cdot C_6H_4 \cdot OMe)_2 \cdot (N \cdot C_6H_4 \cdot OMe)_2$, derived from *p*-anisidine, which crystallises from a mixture of benzene and alcohol in red needles and melts at 242° .

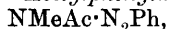
Diazoamino-*p*-phenetole separates from a mixture of ether and light

petroleum in yellowish-brown crystals and melts at 119° (compare Henriques, Abstr., 1893, i, 39). W. A. D.

New Syntheses of Diazoamino-derivatives. IV. OTTO DIMROTH (*Ber.*, 1905, 38, 670—688).—*Phenylmethyltriazen* (diazobenzene-methylamine), N_3HMePh (Abstr., 1903, i, 450), prepared by adding phenylazoimide dissolved in ether to an ethereal solution of magnesium methyl iodide, and mixing at 0° the product with an aqueous solution of ammonium chloride containing ammonia, crystallises in long prisms, melts at 37 — 37.5° , and begins to decompose at 90° ; it can, however, be distilled in a vacuum or by means of steam, and boils at 120° under 20 mm. pressure. The *silver* derivative, $N_3AgMePh$, crystallises from benzene on adding light petroleum and is rapidly decomposed by acids, nitrogen being evolved; the *cuprous* derivative forms large, orange prisms and begins to decompose at 180° . The following facts show that phenylmethyltriazen is capable of existing in the two isodynamic forms, $NHPh \cdot N_2Me$ and $NPh \cdot N \cdot NHMe$, between which it is impossible to discriminate. With acids at 0° , decomposition occurs exclusively in the direction of the equation $NMe \cdot N \cdot NHPh + 2HCl = MeCl + N_2 + NH_2Ph, HCl$, the theoretical quantity of aniline being formed. That this result does not occur in the following manner, (1) $NHMe \cdot N_2Ph + 2HCl = NH_2Me, HCl + N_2PhCl$; (2) $N_2PhCl + NH_2Me, HCl = NH_2Ph, HCl + MeCl + N_2$, is shown by the fact that a solution of benzenediazonium chloride is absolutely unaffected by methylamine hydrochloride at 0° . Phenylmethyltriazen is, moreover, decomposed by anhydrous hydrogen chloride in benzene solution, giving aniline only; it is also readily decomposed by acetic acid and by aqueous carbon dioxide. With phenylcarbimide, *s*.-phenylmethylcarbamidoazobenzene,



is obtained; it crystallises from alcohol in lustrous, pale yellow needles, melts at 104° , and is quantitatively resolved by hydrogen chloride in benzene solution into *s*.-phenylmethylcarbamide and benzenediazonium chloride. *Acetylphenylmethyltriazen*,



prepared by the action of acetic anhydride on phenylmethyltriazen dissolved in pyridine at 0° , separates from light petroleum in colourless, lanceolate crystals and melts at 35° . Attempts to methylate phenylmethyltriazen have as yet not been successful. Benzenediazonium chloride in alcohol at 0° converts it into *bisdiazobenzene*methylamide, $NMe(N_2Ph)_2$.

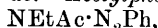
Phenylmethyltriazen is reduced by zinc dust and ammonia principally to phenylhydrazine, but small quantities of aniline are obtained; reduction with sodium amalgam, however, gives rise to aniline and hydrazine.

Phenylethyltriazen, N_3HEt_2Ph , prepared from phenylazoimide and magnesium ethyl iodide, separates from light petroleum in thick crystals and melts at 31° ; the crystalline *silver* derivative, $C_8H_{10}N_3Ag$, melts at 115° and the analogous *cuprous* derivative melts at 141° . It is decomposed by acids in the same way as the corresponding methyl derivative. With phenylcarbimide, it gives *s*.-ethyl-phenylcarbamidoazobenzene, $NHPh \cdot CO \cdot NEt \cdot N \cdot NPh$, which crystallises

from alcohol in silky needles, melts at 99° , and is decomposed by hydrogen chloride in ethereal solution, giving phenylethylcarbamide,



and benzenediazonium chloride. *Acetylphenylethyltriazen*,



crystallises from light petroleum and melts at 26° .

The same phenylbenzyltriazen, $\text{N}_3\text{HPh}\cdot\text{CH}_2\text{Ph}$, is obtained either by acting on phenylazoimide with magnesium benzyl chloride or by treating benzylazoimide with magnesium phenyl bromide. Its formation therefore corresponds with the two isodynamic formulæ, $\text{NHPh}\cdot\text{N}_2\cdot\text{CH}_2\text{Ph}$ and $\text{NPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$. With hydrochloric acid at 0° , moreover, it gives solely aniline hydrochloride and benzyl chloride, corresponding with the first formula, but, as stated by Goldschmidt and Holm (Abstr., 1888, 685), it behaves with phenylcarbimide as if it had the second of the two formulæ.

Benzylmethyltriazen, $\text{N}_3\text{HMe}\cdot\text{CH}_2\text{Ph}$, is the first diazoamino-compound prepared containing the nitrogens combined on both sides with alkyl groups; prepared by the action of magnesium methyl iodide on benzylazoimide, it is purified by distillation and subsequent conversion into its silver derivative, the latter being then decomposed by alkaline aqueous sodium sulphide. It forms a colourless liquid which does not solidify on strongly cooling, decomposes slightly when distilled at $110\text{--}130^{\circ}$ under 20 mm. pressure, and is very readily decomposed by acids, even by aqueous carbon dioxide, giving off the whole of its nitrogen. The *silver* derivative, $\text{C}_8\text{H}_{10}\text{N}_3\text{Ag}$, crystallises from ether in colourless, prismatic needles and melts at 125° ; the *cuprous* derivative, $\text{C}_8\text{H}_{10}\text{N}_3\text{Cu}$, is also crystalline and melts at 114° .

W. A. D.

Diastasic Coagulation of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1905, 140, 95—97. Compare Abstr., 1903, i, 679; 1904, i, 211, 228, 294, 374; this vol., i, 164).—Malt extract which has been heated to destroy the amylocoagulase is still capable of causing diastasic coagulation in starch paste, and this affords further evidence in favour of the theory already advanced by the authors, namely, that in the diastasic formation of amylocellulose the coagulation is started by the diastase and then proceeds spontaneously (Abstr., 1904, i, 374). The formation of amylocellulose is stopped altogether either by adding to the starch paste excess of malt extract or by keeping it at a temperature of 60° ; in each case, complete saccharification (liquefaction) is produced. Experiments conducted on starch paste which had been strongly heated under pressure showed that the state of liquefaction favourable to coagulation is equally favourable to the diastasic formation of amylocellulose.

M. A. W.

Organic Chemistry.

Composition of Petroleum CHARLES F. MABERY. I. Hydrocarbons in Ohio Trenton Limestone Petroleum. CHARLES F. MABERY and O. H. PALM. II. Hydrocarbons in Canadian Petroleum with High Boiling Points. III. Hydrocarbons in Santa Barbara Crude Oil. IV. Separation of Solid Paraffin Hydrocarbons from Petroleum without Distillation. CHARLES F. MABERY and OTTO J. SIEPLEIN. V. The Solid Paraffin Hydrocarbons that collect in Oil Wells in Pennsylvania. VI. Composition of Commercial Paraffin. VII. Composition of Commercial Vaseline, Cosmoline, and Similar Products (*Amer. Chem. J.*, 1905, 33, 251—292).—I. It has been shown previously (Abstr., 1897, i, 449) that the distillate, boiling at 212—214°, from Ohio Trenton limestone petroleum consists of dodecane, $C_{12}H_{26}$. A study has now been made of the higher boiling portions of the oil, and a number of hydrocarbons have been isolated by filtering the various fractions at -10° and purifying the filtrates by treatment with fuming sulphuric acid. The results show that Ohio petroleum consists mainly of hydrocarbons of the series C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} , and C_nH_{2n-4} , and resembles Pennsylvania petroleum in containing a large proportion of solid hydrocarbons.

The following hydrocarbons have been separated, and their sp. gr. and refractive indices determined :

Series.	Formula.	From fraction boiling at	Sp. gr. at 20°.	Refractive index.
C_nH_{2n} ...	$C_{12}H_{24}$	211—213° under atmospheric pressure	0.7970	1.4350
" ...	$C_{13}H_{26}$	223—225 " " "	0.8055	1.4400
" ...	$C_{14}H_{28}$	138—140 " 30 mm. "	0.8129	1.4437
" ...	$C_{15}H_{30}$	152—154 " " "	0.8204	1.4480
" ...	$C_{16}H_{32}$	164—168 " " "	0.8254	1.4510
" ...	$C_{17}H_{34}$	177—179 " " "	0.8335	1.4545
C_nH_{2n-2} ...	$C_{19}H_{36}$	198—202 " " "	0.8471	1.4614
" "	$C_{21}H_{40}$	213—217 " " "	0.8546	1.465
" "	$C_{22}H_{42}$	224—227 " " "	0.8614	1.4690
" "	$C_{24}H_{46}$	237—240 " " "	0.8639	1.4715
C_nH_{2n-4} ...	$C_{23}H_{42}$	253—255 " " "	0.8842	1.4797
" "	$C_{24}H_{44}$	263—265 " " "	0.8864	1.4802
" "	$C_{25}H_{46}$	275—278 " " "	0.8912	1.4810

II. The constituents of Canadian Corniferous limestone petroleum which distil below 196° have been shown (*loc. cit.*) to be members of the series C_nH_{2n+2} , whilst above this temperature members of the series C_nH_{2n} appear. By distilling the higher fractions the following hydrocarbons have been separated.

The hydrocarbon, $C_{12}H_{24}$, boils at 216° ; its *chloro*-derivative, $C_{12}H_{23}Cl$, boils at 160° under 15 mm. pressure and has a sp. gr. 0.9145 at 20° . The hydrocarbon, $C_{13}H_{26}$, boils at 228 — 230° under 15 mm. pressure and has a sp. gr. 0.7979 at 20° and n_D 1.444; the *chloro*-derivative, $C_{13}H_{25}Cl$, boils at 165° under 15 mm. and has a sp. gr. 0.9221 and n_D 1.465. The hydrocarbon, $C_{14}H_{28}$, boils at

141—143° under 50 mm. pressure and has a sp. gr. 0.8099 at 20° and n_D 1.449; the *chloro*-derivative, $C_{14}H_{27}Cl$, boils at 180° under 15 mm. pressure and has a sp. gr. 0.9288 at 20° and n_D 1.471; the *dichloro*-derivative, $C_{14}H_{26}Cl_2$, boils at 197—200° under 15 mm. and has a sp. gr. 1.0066 at 20° and n_D 1.489. The hydrocarbon, $C_{15}H_{30}$, boils at 159—160° under 60 mm. pressure and has a sp. gr. 0.8192 at 20° and n_D 1.452; the *chloro*-derivative, $C_{15}H_{29}Cl$, boils at 190° under 15 mm. pressure and has a sp. gr. 0.9358 at 20° and n_D 1.455.

III. A sample of crude petroleum from Santa Barbara County, Cal., which was of particular interest owing to its heavy, viscous character, was examined with the following results.

The oil had a sp. gr. 0.9845 at 20°, and the following composition: S, 0.84 per cent.; N, 1.25 per cent.; C, 86.32 per cent.; H, 11.70 per cent. The lower boiling fractions of the oil were found to consist of hydrocarbons of the series C_nH_{2n-2} , whilst the higher fractions contained hydrocarbons of the C_nH_{2n-4} and C_nH_{2n-8} series.

The following hydrocarbons were separated:

Hydrocarbon.	Boiling point under 60 mm. pressure.	Sp. gr. at 20°.	Refractive index.
$C_{13}H_{24}$	150—155°	0.8621	1.4681
$C_{16}H_{30}$	175—180	0.8808	1.470
$C_{17}H_{30}$	190—195	0.8919	1.4778
$C_{18}H_{32}$	210—215	0.8996	1.484
$C_{24}H_{44}$	250—255	0.9299	—
$C_{27}H_{46}$	310—315	0.9451	1.5146
$C_{29}H_{50}$	340—345	0.9778	—

IV. In order to demonstrate that the solid paraffin hydrocarbons are actually contained in crude petroleum and are not formed by decomposition, a sample of Pennsylvania petroleum was left in a draught of air until the residue ceased to lose weight or change in sp. gr. On cooling the product with ice, it solidified completely. When distilled, 28 per cent. collected below 300°, 6 per cent. below 360°, leaving a residue of 66 per cent. boiling above 360°. The amount of solid hydrocarbons in the residue was estimated by dissolving it in *iso*-amyl alcohol and adding alcohol; the precipitate was collected and extracted with benzene. On evaporating the benzene solution, a greenish-black solid was obtained amounting to 39.6 per cent. of the heavy residue, or 14 per cent. of the original oil before evaporation. By repeated purification, a white substance was obtained which melted at 61°, had a sp. gr. 0.7966 at 70°, and the composition of a paraffin hydrocarbon.

V. The semi-solid product that collects in large quantities in certain oil wells in Pennsylvania has been investigated. The sample examined was a thick paste with sp. gr. 0.8345 at 60°. By fractional distillation and cooling the fraction with a mixture of ice and salt, the following solid hydrocarbons were isolated:

Hydrocarbon.	Formula.	Melting point.	Sp. gr.
Tetracosane	$C_{24}H_{50}$	50—51°	0.7900 at 60°
hentriacontane ...	$C_{31}H_{64}$	66	0.7997 at 70
dotriacontane	$C_{32}H_{66}$	67—68	0.8005 at 75
tetratriacontane ...	$C_{34}H_{70}$	71—72	0.8009 at 80
Pentatriacontane ...	C_3H_{72}	76	0.8052 at 80

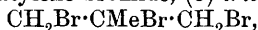
VI. A sample of commercial paraffin was distilled under 40 mm. pressure; the distillates collected between 250° and 350°, leaving a residue of only 2 per cent., whence it is evident that the solid hydrocarbons of commercial paraffin are members of the series C_nH_{2n+2} . The following hydrocarbons were isolated:

Hydrocarbon.	Formula.	Melting point.	Sp. gr.
Tri-icosane	$C_{23}H_{48}$	48°	0.7886 at 60°
Tetracosane	$C_{24}H_{50}$	50—51	—
Pentacosane	$C_{25}H_{52}$	53—54	0.7941 at 60
Hexacosane	$C_{26}H_{54}$	55—56	0.7968 at 60
Octacosane	$C_{28}H_{58}$	60	—
Nonacosane	$C_{29}H_{60}$	62—63	—

VII.—An examination of commercial vaseline (Ceroleum) has shown that this substance consists of heavy oils which form the high-boiling portion of Pennsylvania petroleum, hydrocarbons of the series C_nH_{2n} , C_nH_{2n-2} , and C_nH_{2n-4} , together with solid paraffin hydrocarbons.

E. G.

Action of Bromine on *iso*Butylene. S. A. POGORŽELSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1486—1505).—Linnemann and Zotta (this Journal, 1872, 476) only obtained *isobutylene* bromide on the interaction of bromine and *isobutylene*. The compounds isolated by the author as the products of this reaction, carried out under the conditions previously employed (this vol., i, 165) in studying the action of chlorine on *isobutylene*, are as follows: (1) a small quantity of *tert.*-butyl bromide, (2) *isobutylene* bromide, (3) *tribromoisobutane*,



which is a colourless, heavy liquid, boils at 103° under 10 mm. and at 107° under 14 mm. pressure, and has the sp. gr. 2.2329 at 0°/0° and 2.1974 at 21°/0°. When treated with potassium acetate, it yields the *bromide-acetate*, $C_4H_8Br(C_2H_3O_2)$, which is a colourless liquid with a pleasant odour, boils at 193—194° under 766 mm. and at 96—97° under 18 mm. pressure, and has the sp. gr. 1.4278 at 0°/0° and 1.3997 at 22°/0°. Hydrolysis of this ester yields the corresponding *alcohol*, $OH \cdot CH_2 \cdot CMe \cdot CH_2Br$, as a colourless liquid which boils at 181—183° under 752 mm. pressure, has the sp. gr. 1.5611 at 0°/0° and 1.5406 at 18°/0°, and energetically decolorises bromine or potassium permanganate.

In the action of bromine on *isobutylene*, there are no unsaturated compounds formed, as is the case in the interaction of chlorine and *isobutylene* (*loc. cit.*).

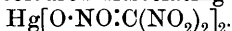
When the products of the action of bromine on *isobutylene* are left in contact with water, α -*isobutylene* oxide is formed (compare Krasusky, *Abstr.*, 1903, i, 8).

The action of bromine on *isocrotonyl* bromide gives the *tribromoisobutane*, $CMe_2Br \cdot CHBr_2$, which boils at 96° under 14 mm. pressure and has the sp. gr. 2.2017 at 0°/0° and 2.1753 at 21°/0°. When treated with potassium acetate, this compound yields the unsaturated dibromide prepared by Norton and Williams (*Abstr.*, 1887, 712).

T. H. P.

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Mercury Nitroform and the Constitution of Salt Solutions. HEINRICH LEY (*Ber.*, 1905, **38**, 973—978).—Mercury nitroform dissolves in ether, benzene and its homologues, ethyl acetate, ethyl oxalate, chloroform, carbon tetrachloride, and lactic acid, giving colourless solutions; with alcohols, aliphatic ketones, acetic acid, dichloroacetic acid and nitriles, feebly yellow solutions are obtained, whilst the solutions in pyridine and water are strongly yellow. The solutions in pyridine and water have a considerable electrical conductivity, which is increased on dilution, especially in the case of water. It is assumed that the colourless solutions contain the compound $\text{Hg}[\text{C}(\text{NO}_2)_3]_2$, and the yellow solutions the coloured dissociating compound



Mercury nitroform combines with triethylamine to form the additive compound $\text{C}_2\text{O}_{12}\text{N}_6\text{Hg}\cdot\text{C}_6\text{H}_{15}\text{N}$, which is so stable that it can be recrystallised from water. W. A. D.

Ferric Ethoxide. PAUL NICOLARDOT (*Compt. rend.*, 1905, **140**, 857—859).—Grimaux (*Abstr.*, 1884, 573) has stated that when sodium ethoxide is added to a solution of anhydrous ferric chloride in absolute alcohol, pure sodium chloride is precipitated and ferric ethoxide remains in solution. The author finds that the precipitate is by no means pure sodium chloride, but that it contains very considerable quantities of iron. The alcoholic solution, moreover, always contains sodium. The conclusion is drawn that ferric ethoxide is not present in the alcoholic solution, and that there is no reason to assume the existence of such a substance. H. M. D.

Esters of Phosphorous Acid. ALEXANDER ARBUSOFF (*Ber.*, 1905, **38**, 1171—1173).—The esters of the type $\text{P}(\text{OR})_3$ which have been hitherto described are really mixtures of the three esters $\text{P}(\text{OR})_3$, $\text{P}(\text{OR})_2\cdot\text{OH}$ and $\text{PO}(\text{OR})_3$. The following substances were obtained pure by a lengthy fractional distillation, under diminished pressure, of the crude products:

Substance.	B. p. under 760 mm.	B. p. under 8—10 mm.	Sp. gr. at 0°.
$\text{P}(\text{OMe})_3$	111—112°	—	1·0790
$\text{P}(\text{OEt})_3$	155—156	49°	0·9777
$\text{P}(\text{OPr}^a)_3$	206—207	83	0·9705
$\text{P}(\text{OPr}^b)_3$	—	60—61	0·9361
$\text{P}(\text{OMe})_2\cdot\text{OH}$	—	56·5	1·2184
$\text{P}(\text{OEt})_2\cdot\text{OH}$	187—188	72	1·0912
$\text{P}(\text{OPr}^a)_2\cdot\text{OH}$	—	91	1·0366
$\text{P}(\text{OPr}^b)_2\cdot\text{OH}$	—	74—75	1·0159
$\text{PO}(\text{OMe})_3$	192—193	72—73	1·2148
$\text{PO}(\text{OEt})_3$	215—216	98—98·5	1·0897
$\text{PO}(\text{OPr}^a)_3$	—	120·5—121·5	1·0282
$\text{PO}(\text{OPr}^b)_3$	—	95—96	1·0054
$\text{PO}(\text{OC}_4\text{H}_9)_3^{\text{iso}}$	—	135—136	0·9698

The esters $\text{P}(\text{OC}_4\text{H}_9)_3$ and $\text{P}(\text{OC}_4\text{H}_9)_2\cdot\text{OH}$, derived from *isobutyl* alcohol, could not be separated; the mixture is a liquid boiling at 103—104° under 9 mm. pressure and having a sp. gr. 0·9275 at 0°/0°.

The esters of the type $\text{P}(\text{OR})_3$ differ from those having the formulæ $\text{P}(\text{OR})_2\cdot\text{OH}$ and $\text{PO}(\text{OR})_3$ by forming definite compounds with the

cuprous haloids. The following table gives the properties of a series of these compounds :

Substance.	CuCl-compound. M. p.	CuBr-compound. M. p.	CuI-compound. M. p.
P(OMe) ₃ , CuX.....	190—192°	180—182°	175—177°
2P(OMe) ₃ , CuX ...	—	—	69—70
P(OEt) ₃ , CuX	Liquid	27—28	109—110
P(OPr ^a) ₃ , CuX ...	Liquid	Liquid	64—65
P(OPr ^β) ₃ , CuX ...	112—114	149—150	184—185
P(OC ₄ H ₉) ₃ , CuX ...	Liquid	Liquid	—
P(OPh) ₃ , CuX.....	95—96	90·5—91·5	—
2P(OPh) ₃ , CuX ...	—	73—77	73—75

W. A. D.

Nomenclature of Compounds of Variable Constitution. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 998—1004).—The author points out the necessity of having a simple and definite nomenclature for compounds which undergo intramolecular changes, and more particularly for acids and pseudo-acids, bases and pseudo-bases.

Examples are quoted to indicate the unsatisfactory nature of the present nomenclature. The author suggests the adoption of the following in the case of pseudo-acids and the isomeric true acids :

(1) If the name at present in use refers to the pseudo-acid, the prefix *aci-* attached to this name will designate the true acid.

The enolic derivatives of aldehydes and ketones would, therefore, according to this system be termed *aci*-aldehydes and *aci*-ketones, for example, *aci*-dibenzoylacetone, *aci*-diketopentamethylene. Ethyl β -hydroxycrotonate is termed ethyl *aci*-acetoacetate ; hydroxymethylene compounds are termed *aci*-formyl compounds ; salts of phenolphthalein are derivatives of *aci*-phenolphthalein ; acid amides and imides give salts of *aci*-amides and *aci*-imides. Many other examples are mentioned.

In the event of this nomenclature being adopted, it would be necessary to alter the nomenclature of the diacipiperazines to diketopiperazines or piperazones.

(2) If the name at present in use refers to the true acid, the prefix *pseudo-* attached to this name will designate the pseudo-acid. Examples of the application of this nomenclature are quoted. Colourless violuric acid is *pseudo*-violuric acid. Cyanuric acid and uric acid are *pseudo*-cyanuric acid and *pseudo*-uric acid respectively on the assumption that they do not possess hydroxyl groups.

It is accordingly necessary to distinguish sharply between *pseudo*- and *iso*-compounds.

A. McK.

Preparation of Acetyl Hydrogen Peroxide. PARKE, DAVIS & Co. (D.R.-P. 156998).—When benzoyl acetyl peroxide is dissolved in water, hydrolysis takes place according to the equation $2\text{OBz}\cdot\text{OAc} + \text{H}_2\text{O} = \text{O}_2\text{Bz}_2 + \text{HOAc} + \text{OAc}\cdot\text{OH}$. The benzoyl peroxide is insoluble, and the solution of acetyl hydrogen peroxide and acetic acid may be employed directly for antiseptic purposes. C. H. D.

Rôle of Sulphuric Acid when Acetylating with Acetic Anhydride. OTTO STILLICH (*Ber.*, 1905, 38, 1241—1246).—By the interaction of concentrated sulphuric acid and acetic anhydride, acetyl sulphuric acid is primarily formed at low temperatures; at higher temperatures, it rapidly changes to sulphoacetic acid. 3-*p*-Nitrophenyl-2-methyl-6-nitrodihydroquinazoline forms a sulphoacetate, decomposing at 268°, and an acetylsulphate decomposing at 213° (compare Abstr., 1903, i, 864).

The *ethyl sulphate* of nitrophenylmethylnitrodihydroquinazoline crystallises in faintly yellow prisms which sinter at 252° and decompose at 257—259°.

Barium sulphoacetate forms hydrogen sulphide, carbon dioxide, and a gas with a marked odour when heated at 350° in a metal bath. Sulphoacetic acid, obtained by decomposing the lead salt with hydrogen sulphide, melts at 84—86° and decomposes at 245°.

E. F. A.

Natural Heptadecoic Acid. DAVID HOLDE, LEO UBBELOHDE, and JULIUS MARCUSSEN (*Ber.*, 1905, 38, 1247—1258).—The heptadecoic acids, melting between 53° and 57°, described as occurring naturally in olive oil (Holde, Abstr., 1903, i, 140), pig fat (Kreis and Hafner, Abstr., 1903, i, 788), datura oil (Gérard, Abstr., 1890, 1395), and palm fat (Nördlinger, *Zeit. angew. Chem.*, 1892, 110), have been subjected to very careful fractionation with magnesium acetate in alcoholic solution and subsequent repeated crystallisation or distillation in a vacuum. They are shown in every case to be a mixture of palmitic, stearic, and other acids containing an even number of carbon atoms.

E. F. A.

Elaidin and Elaidic Acid. GAWALOWSKI (*Chem. Centr.*, 1905, i, 804; from *Pharm. Post*, 38, 97—98).—On applying the elaidin test to a commercial oleic acid having a sp. gr. 0.934, melting point 30.7°, and solidification point 27°, and containing 4 per cent. of unsaponifiable matter, a mixture of a solid and a liquid elaidic acid was obtained at 17°.

The solid acid, amounting to 60 per cent., was nearly colourless and of tallowy odour, and had the sp. gr. 0.930, melting point 38°, and solidification point 23°, and contained 0.3 per cent. of unsaponifiable matter. The liquid acid, amounting to 30 per cent., was colourless and of faint fatty odour, and had the sp. gr. 0.936, melting point 16.5°, solidification point 14.9°, and contained 16.2 per cent. of unsaponifiable matter.

The author designates the solid *stereo-elaidic* and the liquid *oleo-elaidic* acid.

G. D. L.

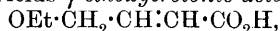
***d*-Lactic Acid.** ÉMILE JUNGFLAISCH and MARCEL GODCHOT (*Compt. rend.*, 1905, 140, 719—721. Compare Abstr., 1904, i, 645, 796).—The racemisation observed when quinine *d*-lactate is converted into the corresponding zinc salt (compare Abstr., 1904, i, 796) is due to the prolonged action of the barium hydroxide, and can be avoided by using cold saturated solutions of the salt and reagents in equiva-

lent quantities; crystalline zinc *d*-lactate thus prepared has the composition $\text{Zn}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$, and the rotatory power of its aqueous solutions increases with the dilution, solutions containing 5.0, 2.5, 1.25, and 0.512 grams of salt per 100 c.c. of solution have $[\alpha]_D - 6.0^\circ$, -8.0° , -11.1° , and -13.35° respectively at 15° . *d*-Lactic acid, obtained by Krafft and Dijes' method (Abstr., 1896, i, 84) or by a more simple process not yet described, crystallises in radiating clusters of prismatic needles melting at $25-26^\circ$, or 7° or 8° higher than the racemic acid; aqueous solutions of the pure acid are dextrorotatory, the value of $[\alpha]_D$ diminishing as the dilution increases, thus solutions containing 10.458, 5.022, 2.511, or 1.527 grams of $\text{C}_3\text{H}_6\text{O}_3$ per 100 c.c. have $[\alpha]_D + 3.82^\circ$, $+3.33^\circ$, $+2.67^\circ$, or $+2.61^\circ$ respectively at 15° . Wislicenus (compare Abstr., 1873, 57; 1874, 249; 1876, 561) also observed the variation of $[\alpha]_D$ with the concentration in the case of *d*-lactic acid and its zinc salt, but as he employed concentrated solutions which had been made for some time, it is probable that the changes in the rotation were due to the presence of *d*-lactyl-lactic acid which the author has shown to be formed when aqueous solutions of *d*-lactic acid are evaporated, and has $[\alpha]_D - 150^\circ$; and not, as suggested by Wislicenus, to the presence of the *d*-lactide, which has $[\alpha]_D - 300^\circ$.

Correction.—The values for $[\alpha]_D$ given previously (compare Abstr., 1904, i, 796) are not correct and require to be multiplied by the factor 4.332.

M. A. W.

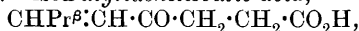
Ethoxycrotonic Acid and Ethylerythritic Acid. ROBERT LESPIEAU (*Compt. rend.*, 1905, 140, 723–724).—*Ethyl γ-ethoxycrotonate*, $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{Et}$, obtained by distilling under reduced pressure ethyl β -hydroxy- γ -ethoxybutyrate (compare this vol., i, 255) with phosphoric oxide, boils at $201-203^\circ$ under 760 mm. pressure, and on saponification yields *γ-ethoxycrotonic acid*,



a colourless, crystalline solid melting at 45° , boiling at $145-146^\circ$ under 26 mm. pressure, and dissolving in ether, light petroleum, benzene, or alcohol. *α-Cyano-γ-ethoxypropylene* (γ -ethoxycrotononitrile), $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CN}$, obtained by distilling β -hydroxy- γ -ethoxybutyronitrile with phosphoric oxide, is a colourless liquid which boils at $190-191^\circ$ under 750 mm. pressure, solidifies in liquid methyl chloride, and readily combines with 1 mol. of hydrogen chloride. *γ-Ethylerythritic acid*, $\text{OEt} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_2 \cdot \text{CO}_2\text{H}$, obtained by oxidising barium γ -ethoxycrotonate with barium permanganate at 0° , crystallises from benzene and melts at $90-92^\circ$.

M. A. W.

Condensation of Lævulic Acid with *iso*Butaldehyde. FRITZ MEINGAST (*Monatsh.*, 1905, 26, 265–277).—When boiled with dilute sodium hydroxide in a reflux apparatus, *isobutaldehyde* and *lævulic acid* condense to form *isobutylidenelævulic acid* and octoglycol (Fossek, Abstr., 1884, 832). *isoButylidenelævulic acid*,



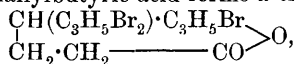
is a yellow, odourless oil, which decomposes at about 230° under 10 mm. pressure, and with bromine in chloroform solution forms an

unstable dibromide. The calcium, $(C_9H_{13}O_3)_2Ca$, and the silver, $C_9H_{13}O_3Ag$, salts were analysed; the ethyl ester, formed from the acid by the action of alcohol and sulphuric acid, is a yellow liquid which boils at $150-155^\circ$ under 16 mm. pressure. In aqueous sodium carbonate solution, isobutylidenelævulic acid is oxidised by permanganate in the cold to isobutyric and succinic acids. G. Y.

Acetyl-lactic [α -Acetoxypionic] Acid. VICTOR AUGER (*Compt. rend.*, 1905, 140, 938-939).— α -Acetoxypionic acid, prepared by heating calcium lactate or lactic acid with acetyl chloride, or lactic acid with acetic anhydride, forms colourless, deliquescent crystals, melting at $39-40^\circ$ and boiling at $167-170^\circ$ under 78 mm. or $148-150^\circ$ under 50 mm. pressure; its aqueous solution is stable, but as it is readily hydrolysed by metallic hydroxides, even in the cold, it is not possible to prepare its salts in a pure state. An attempt to prepare the acid by the hydrolysis of ethyl α -acetoxypionate (compare Wislicenus, *Annalen*, 1863, 75, 61) was unsuccessful, and the compound melting at 166° , obtained by Siegfried (compare Abstr., 1890, 128) from meat extract, was probably a polymeride or stereoisomeride of the acid described above. M. A. W.

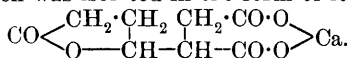
Action of Allyl Iodide on Ethyl Succinate in presence of Zinc. γ -Diallylbutyrolactone. ALEXANDER KASANSKY (*J. pr. Chem.*, 1905, [ii], 71, 249-257).—A mixture of 1 mol. of ethyl succinate and 2 mols. of allyl iodide was added to a mixture of finely granulated zinc and ether in a retort cooled by ice; after one month, water was added and the product extracted with ether and distilled. The fraction boiling at $244-250^\circ$ contained ethyl γ -hydroxy- γ -diallylbutyrate; that boiling at $250-270^\circ$ contained γ -diallylbutyrolactone.

γ -Diallylbutyrolactone, $CH_2 \begin{smallmatrix} \diagup C(C_3H_5)_2 \\ \diagdown CH_2 \cdot CO \end{smallmatrix} O$, is a viscid liquid which boils at $266-267^\circ$, and with aqueous alkali hydroxides, baryta, or calcium hydroxide yields the corresponding salts of γ -hydroxy- γ -diallylbutyric acid. With bromine in carbon tetrachloride solution, the lactone forms a tetrabromide, $C_4H_4O_2(C_3H_5Br_2)_2$, which crystallises in long, thin, white, rectangular plates, melts at $125-127^\circ$, and is highly refractive. With hydrogen iodide, under cooling, the lactone forms γ -iodo- γ -diallylbutyric acid, $C(C_3H_5)_2I \cdot CH_2 \cdot CO_2H$, which is an oil, and is reduced by sodium amalgam in alcoholic sulphuric acid to γ -diallylbutyric acid. This is a liquid which boils at $264-267^\circ$; the sodium and silver salts are described. With bromine in carbon tetrachloride solution, γ -diallylbutyric acid forms a tribromolactone,



a reddish-brown, viscid liquid which fumes when anhydrous.

The oxidation of γ -diallylbutyrolactone by potassium permanganate in aqueous solution, under cooling, leads to the formation of a dibasic lactonic acid, which was isolated in the form of its calcium salt,



G. Y.

Influence of the Ethylenic Linkage in an [Optically] Active Molecule. JULES MINGUIN (*Compt. rend.*, 1905, 140, 946—948).—The increased rotatory power of those derivatives of optically active substances which contain an ethylenic linkage has already been observed by Haller (Abstr., 1891, 1498; 1903, i, 503, 563, 628), Haller and Muller (Abstr., 1899, ii, 622), Eijkmann (Abstr., 1891, 919), Zelinsky (Abstr., 1902, i, 2, 597), Rupe (Abstr., 1903, i, 565), and by the author (Abstr., 1903, i, 428; 1904, i, 330; this vol., i, 130), and in the present paper it is shown that the esters of amyl alcohol or borneol have rotations which vary with the nature of the acid, being higher in the case of the unsaturated than in the case of the saturated acids. Amyl succinate, maleate, and fumarate gave $\alpha +9^{\circ}0'$, $+11^{\circ}30'$, $+15^{\circ}40'$ respectively in 20 cm. tubes, and amyl butyrate and crotonate gave $\alpha +2^{\circ}46'$ and $+3^{\circ}30'$ in 10 cm. tubes (compare Guye, Abstr., 1895, i, 202, 318; Walden, Abstr., 1897, ii, 3). These esters were prepared by heating amyl alcohol and the corresponding acid, and the amyl alcohol regenerated from the esters was identical in optical activity with the original. Bornyl succinate and fumarate in alcoholic solution, 0.392 gram in 25 c.c. of alcohol, gave $\alpha -1^{\circ}22'$ and $-1^{\circ}42'$ respectively in 20 cm. tubes, and bornyl butyrate and crotonate in alcoholic solution, 1.40 gram in 25 c.c. of alcohol, gave $\alpha -4^{\circ}30'$, $-4^{\circ}44'$ respectively in 20 cm. tubes. M. A. W.

Action of Sulphuric Acid on Organic Acids. WILLIAM OECHSNER DE CONINCK and RAYNAUD (*Chem. Centr.*, 1905, i, 671; from *Rev. gen. Chim. pure appl.*, 8, 61—62. Compare Abstr., 1903, i, 231, 457).—A higher acid containing a CH group is less stable towards hot sulphuric acid than one having a CH₂ group; a larger number of CH₂ groups or a longer chain also diminishing the stability. When the acids are gradually heated with an excess of glycerol, the gases evolved being led through concentrated sulphuric acid, sebacic acid gives a little carbon dioxide, glutaric and suberic acids are not decomposed, but the sulphuric acid becomes brownish-red and orange-red respectively. Ethyl-, methylethyl-, and isopropyl-malonic acids readily yield carbon dioxide; methylmalonic acid and its ethyl ester decompose more easily, alcohol and propionic acid being also formed from the latter substance. Anisic acid is not decomposed, but the sulphuric acid is coloured bright red; mucic and quinic acids are slowly decomposed, Bordeaux and reddish-pink colours respectively being produced. Alcohol is given off and a wine-red coloration of the acid produced by ethyl formate, ethyl acetate being equally stable. G. D. L.

Dimethyladipic and Trimethyladipic Acids. WILLIAM A. NOYES and HOWARD W. DOUGHTY (*Ber.*, 1905, 38, 947—950. Compare Abstr., 1901, i, 631).—The acids previously described as di- and tri-methyl adipic acids are now shown to be respectively β -isopropyl- and α -methyl- β -isopropyl-glutaric acids (Blanc, Abstr., 1904, i, 647; Howles, Thorpe, and Udall, *Trans.*, 1900, 77, 942). A claim for priority in obtaining compounds with a trimethylcyclopentane ring from camphor is made (compare Perkin and Thorpe, *Trans.*, 1904, 85, 128). J. J. S.

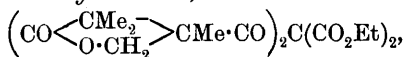
Camphoric Acid. XIV. Derivatives of Trimethylparaconic Acid. WILLIAM A. NOYES (*Amer. Chem. J.*, 1905, 33, 356—365. Compare Noyes and Patterson, *Abstr.*, 1902, i, 741).—An improved method is described for the preparation of trimethylparaconic acid.

When diethyl trimethylitamalate is treated with phosphorus tribromide, *ethyl trimethylparaconate* is produced, which crystallises in needles, melts at 34—35°, and boils at 150—152° under 23 mm. pressure. *Trimethylparaconyl chloride*, $\text{O} \begin{array}{c} \text{CO}-\text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe} \cdot \text{COCl} \end{array}$, is a crystalline substance which melts at 139—140° and is only slowly decomposed by water. The *amide* melts at 241—243° and is sparingly soluble in water, alcohol, ether, or benzene. When trimethylparaconic acid is heated with excess of barium hydroxide solution, *barium trimethylitamalate* is produced. If trimethylparaconyl chloride is heated with bromine in a sealed tube, the corresponding *bromide* is obtained, which melts at 125°, is sparingly soluble in ether, and when heated with alcohol at 230° yields ethyl trimethylparaconate together with the free acid.

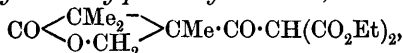
An attempt was made to prepare ethyl hydroxytrimethyladipate lactone by the electrolysis of a mixture of potassium trimethylparaconate and potassium ethyl succinate, but the product consisted of a mixture of esters containing a large proportion of ethyl adipate together with a small quantity of *aa-dimethyl-β-methylenebutyrolactone*, $\text{O} \begin{array}{c} \text{CO}-\text{CMe}_2 \\ \text{CH}_2 \cdot \text{C} : \text{CH}_2 \end{array}$, which is an oily substance, volatile with steam, sparingly soluble in water, and instantly oxidised by potassium permanganate; the *silver* salt of the corresponding hydroxy-acid was prepared and analysed.

aaβ-Trimethylbutyrolactone, $\text{O} \begin{array}{c} \text{CO}-\text{CMe}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{array}$, obtained by the reduction of ethyl trimethylparaconate, melts at 37° and boils at 211—212°; the *silver* salt of the corresponding hydroxy-acid was prepared and analysed.

By the action of trimethylparaconyl chloride on ethyl sodiomalonate, *ethyl ditrimethylparaconylmalonate*,



is obtained, which forms small, compact crystals and melts at 162—163°, together with *ethyl trimethylparaconylmalonate*,



which boils at 250—255° under 60 mm. pressure and is converted by concentrated sodium hydroxide solution into a sparingly soluble *sodium* salt.

By the action of acetic anhydride on barium trimethylitamalate, *acetyltrimethylitamalic anhydride*, $\text{CO} \begin{array}{c} \text{CMe}_2 \\ \text{O} \cdot \text{CO} \end{array} \text{CMe} \cdot \text{CH}_2 \cdot \text{OAc}$, is produced, which boils at 185—195° under 20 mm. pressure; *trimethylparaconic anhydride*, $\left(\text{CO} \begin{array}{c} \text{CMe}_2 \\ \text{O} \cdot \text{CH}_2 \end{array} \right)_2 \text{O}$, which is also pro-

duced in this reaction, forms small, granular crystals, melts at 154—155°, and can also be prepared by boiling trimethylparaconic acid with acetic anhydride. E. G.

Combination of Hydrogen Bromide with Itaconic Anhydride.

LONGINUS ILSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 116—118).—The action of hydrogen bromide on itaconic anhydride in chloroform solution and in complete absence of water yields: (1) bromopyrotartaric acid, melting at 134—135°, and (2) *bromopyrotartaric anhydride*,

$\text{CH}_2\text{Br}\cdot\text{CH}\begin{matrix} \text{CO}-\text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CO} \end{matrix}$, which separates from chloroform in crystals

melting at 55—56° and has the normal molecular weight in freezing acetic acid. T. H. P.

Action of Methyl and Ethyl Chloro-oxalates on Cyanoacetic Esters.

R. TRIMBACH (*Bull. Soc. chim.*, 1905, [iii], **33**, 372—375).—Ethyl cyano-oxalacetate, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, prepared by the action of ethyl chloro-oxalate on the sodium derivative of ethyl cyanoacetate, melts at 96° (compare Bertini, *Abstr.*, 1901, i, 776). *Methyl ethyl cyano-oxalacetate*, $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, similarly obtained from methyl cyanoacetate, melts at 102°. The *ethyl propyl ester*, $\text{CO}_2\text{Pr}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, melts at 59° and the analogous *ethyl isobutyl ester* at 58°.

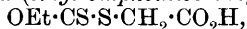
Methyl cyano-oxalacetate, $\text{CO}_2\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}$, prepared by the action of methyl chloro-oxalate on methyl cyanoacetate, melts at 108°, the *methyl ethyl ester*, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Me}$, at 85°, and the *methyl propyl* and *methyl isobutyl esters* at 73° and 65° respectively.

T. A. H.

Ester-acids of Sulphur-substituted Carbonic Acids with Aliphatic Hydroxy-acids.

B. HOLMBERG (*J. pr. Chem.*, 1905, [ii], **71**, 264—295. Compare Tröger and Volkmer, this vol., i, 15; Biilmann, *Dissert.*, Copenhagen, 1904).—*Diethyl xanthoformate*, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CO}_2\text{Et}$, is formed by the action of potassium xanthate on ethyl chlorocarbonate, in aqueous solution, cooled by ice. On distilling the product under reduced pressure, a crystalline residue, probably diethyl xanthosulphoformate (Welde, this Journal, 1877, ii, 314), is obtained. Diethyl xanthoformate is a yellow oil, which boils at 133° under 18 mm., or at 149° under 50 mm. pressure, and has a sp. gr. 1.180 at 20°/4° and n_D^{20} 1.527 at the laboratory temperature.

Ethyl xanthoacetic acid (ethyl sulphothiocarboglycollic acid),



is obtained in the form of its *potassium salt* by the action of potassium ethyl xanthate on potassium chloroacetic acid in cooled aqueous solution. The acid crystallises in long, colourless prisms, melts at 57.5—58°, and has, with $\mu_\infty = 378$, a conductivity K 0.0649. The *sodium*, *calcium* (with $4\text{H}_2\text{O}$), *barium* (with $1\frac{1}{2}\text{H}_2\text{O}$), and *magnesium* (with $4\text{H}_2\text{O}$) salts are described. The methyl ester, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ (Tröger and Volkmer, *loc. cit.*), boils at 154° under 24 mm. pressure and has a sp. gr. 1.218 at 20°/4°, and n_D^{20}

1.535. *Diethyl xanthoacetate*, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is a yellow oil, which boils at 157° under 20 mm. pressure and has a sp. gr. 1.179 at $20^\circ/4^\circ$, and n_{Na} 1.523. With potassium hydroxide in alcoholic solution, ethyl xanthoacetic acid yields potassium ethyl thiocarbonate, $\text{OEt}\cdot\text{CO}\cdot\text{SK}$, and potassium thioglycollate. When heated in aqueous solution on the water-bath, potassium ethyl xanthoacetic acid yields potassium thioglycollate, ethyl alcohol, carbon dioxide, and hydrogen sulphide; if the solution is cooled before the evolution of gas has ceased, the intermediate product, trithiocarbodiglycollic acid, is obtained. With aqueous ammonia at the ordinary temperature, ethyl xanthoacetic acid yields xanthamide and thioglycollic acid.

Methyl xanthoacetic acid, $\text{OMe}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained in the form of its *potassium* salt by the action of potassium methyl xanthate on potassium chloroacetate. The acid crystallises in colourless needles, melts at 38° , and is decomposed by water or potassium hydroxide in a similar manner to ethyl xanthoacetic acid. The *barium* salt (with $4\text{H}_2\text{O}$) crystallises in plates; the *ethyl* ester, $\text{OMe}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is a yellow oil, which boils at 158° under 32 mm. pressure and has a sp. gr. 1.225 at $20^\circ/4^\circ$ and n_{Na} 1.535.

Ethyl xantho- α -propionic acid (Tröger and Volkmer, *loc. cit.*), from potassium ethyl xanthate and potassium α -bromopropionate, crystallises in small, colourless, prismatic plates and melts at 49° ; the *calcium* salt, $(\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CHMe}\cdot\text{CO}_2)_2\text{Ca}\cdot 2\text{H}_2\text{O}$, crystallises in colourless, prismatic needles. Trithiocarbodilactic and thiolactic acids are formed by the action of hot water on ethyl xantho- α -propionic acid and its salts.

Ethyl xantho- β -propionic acid, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, obtained from β -iodopropionic acid and potassium xanthate, crystallises in colourless, prismatic needles, and, when acted on by ammonia, yields β -thiolactic acid and β -dithiodilactic acid, which melts at $156\text{--}157^\circ$. The *sodium* ($+3\text{H}_2\text{O}$) and the *calcium* ($+3\text{H}_2\text{O}$) salts are described.

The action of ethyl chlorocarbonate on potassium trithiocarbonate in aqueous solution leads to the formation of ethyl thiodicarbonate, $(\text{OEt}\cdot\text{CO})_2\text{S}$ (Meyer, *Ber.*, 1869, 2, 297), which boils at 119° under 24 mm. pressure, has a sp. gr. 1.123 at $20^\circ/4^\circ$, and, when shaken with aqueous ammonia of sp. gr. 0.90, yields hydrogen sulphide and urethane.

Trithiocarbodiglycollic acid, $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, is formed by the action of potassium chloroacetate on potassium trithiocarbonate in aqueous solution, cooled by water, and addition of sulphuric acid to the product. It crystallises in thin, yellow leaflets or in rhombic plates and melts at $173.5\text{--}174^\circ$. The *potassium*, *sodium* ($+3\text{H}_2\text{O}$), *sodium hydrogen* ($+3\text{H}_2\text{O}$), *calcium* ($+ \text{H}_2\text{O}$), and *barium* ($1\frac{1}{2}\text{H}_2\text{O}$) salts are described. The methyl ester crystallises in long, yellow, prismatic plates and melts at 32° ; the *ethyl* ester crystallises in thin, glistening, yellow needles and melts at 47° . When boiled in neutral or alkaline aqueous solution, the acid yields thioglycollic acid and thiocarbamide; with alcoholic ammonia, the methyl ester yields *thioglycollamide*, $\text{SH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, which crystallises in thin, white leaflets and melts at 149° .

Dithiocarbodiglycollic acid, $\text{CO}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, is formed by the

oxidation of the trithio-acid with potassium permanganate in aqueous potassium carbonate solution, cooled by ice, or by nitric acid of sp. gr. 1.40. It crystallises in thin leaflets, melts at 156° , and decomposes slowly in boiling water, more quickly in aqueous sodium carbonate solution, with formation of thioglycollic acid. The *sodium*, *sodium hydrogen* (with $3\text{H}_2\text{O}$), and *barium* (with $2\frac{1}{2}\text{H}_2\text{O}$) salts are described; the *ethyl* ester, obtained by oxidation of ethyl trithiocarbodiglycolate with nitric acid, crystallises in slender, white needles and melts at 49° .

Sulphothiocarbodiglycollic acid, $\text{OH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was obtained by shaking carbon disulphide with an aqueous solution of potassium glycolate and treating the reaction product with chloroacetic acid. It crystallises in yellow plates and melts at 136° . The *sodium hydrogen* salt crystallises in thick, yellow plates; the *ethyl* ester forms stout, yellow needles and melts at $34\text{--}35^{\circ}$. When heated with water on the water-bath, the acid yields trithiocarbodiglycollic, glycollic, and thioglycollic acids, carbon dioxide, and hydrogen sulphide.

Trithiocarbodilactic acid, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$, formed by the action of α -bromopropionic acid on potassium trithiocarbonate in aqueous solution, is obtained in a yellow crystalline and a liquid modification, which gradually changes into the crystalline form.

Contrary to Biilmann's statement (*loc. cit.*), the successive action of hydrogen sulphide and carbon disulphide on potassium hydroxide in alcoholic solution leads to the formation of potassium trithiocarbonate and potassium xanthate.

G. Y.

Presence and Formation of Formaldehyde in Various Combustions. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1905, [iii], 33, 386—393).—Many of the results recorded in this paper have already appeared (Abstr., 1904, i, 713, and this vol., ii, 53). In the combustion of coal, peat, and various woods in cast-iron stoves, larger amounts of formaldehyde are produced than when these materials are burned in glass vessels. Soot contains varying quantities of trioxymethylene or paraformaldehyde. Formaldehyde is present in the gaseous products obtained by the incomplete combustion of oils, petroleum, and acetylene, and is formed during the combustion of sugar, juniper berries, incense, and other materials which have occasionally been employed in fumigation.

T. A. H.

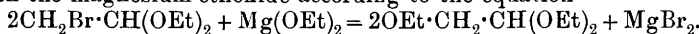
Presence of Formaldehyde in the Atmosphere of Towns. AUGUSTE TRILLAT (*Bull. Soc. chim.*, 1905, [iii], 33, 393—395. Compare preceding abstract; Henriet, Abstr., 1902, i, 714; 1903, i, 600; 1904, i, 289 and 649).—One hundred cubic metres of air examined on two different occasions on the roof of the Pasteur Institute yielded 24 and 17 mg. of formaldehyde respectively. The same quantities of air, collected half-way up the building, yielded respectively 31 and 25 mg. of the aldehyde, whilst from similar samples of air collected at Courbevoie 55 and 25 mg. respectively were obtained. Formaldehyde can be detected in air by exposing a slip of paper tinted

with rosaniline hydrochloride, which in presence of the aldehyde develops a blue colour.

T. A. H.

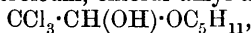
Bromoacetal. PAUL FREUNDLER and LEDRU (*Compt. rend.*, 1905, 140, 794—796. Compare Abstr., 1892, 1424).—When acetal is treated with bromine in presence of calcium carbonate, the yield of bromoacetal is only about 50 per cent. of that required by theory. The chief by-product is bromoacetaldehyde, which is probably formed by hydrolysis of the bromoacetal. In order to improve the method of preparation, it is found advantageous to treat the product of bromination with a 2·5 per cent. solution of hydrobromic acid in alcohol. From 100 parts of acetal, 115 parts of bromoacetal can be thus obtained. Amongst the products of the reaction a small quantity of an oil boiling at 135·5—136·5° under 12—13 mm. pressure was found, which is probably a polymerised bromoacetaldehyde, for it dissociates at the ordinary temperature with the formation of the latter substance.

Bromoacetal is also formed by acting on paraldehyde with bromine at -5° to 0° and treating the product with excess of absolute alcohol. Tetrabromobutaldehyde, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CBr}_2\cdot\text{COH}$, is formed as a by-product in this reaction. *Bromomethyl acetal*, $\text{CH}_2\text{Br}\cdot\text{CH}(\text{OMe})_2$, obtained in similar manner, boils at 53·5—54° under 21 mm. pressure. In alkaline solution, the bromine atom in the bromoacetals is readily replaced by the amino-, hydroxyl, or alkoxyl groups. When treated with finely divided magnesium at 110—115°, reaction takes place according to the equation $2\text{CH}_2\text{Br}\cdot\text{CH}(\text{OEt})_2 + 2\text{Mg} = 2\text{CH}_2\cdot\text{CH}\cdot\text{OEt} + \text{MgBr}_2 + \text{Mg}(\text{OEt})_2$, and on further warming, the remaining bromoacetal reacts with the magnesium ethoxide according to the equation



H. M. D.

Action of Amyl Alcohol on Chloral Ethyl-alcoholate. JOHANNES GADAMER (*Arch. Pharm.*, 1905, 243, 30).—When chloral ethyl-alcoholate, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{OEt}$, is dissolved in amyl alcohol, the excess of the latter driven off at a gentle heat, and the syrupy residue crystallised from chloroform and light petroleum, chloral amyl-alcoholate,



is obtained.

Attention is drawn to the analogy between this behaviour and that of certain substances denominated hydroxydihydro-bases (Decker, Abstr., 1893, i, 115); these must be supposed to react in a tautomeric aldehydic form (compare this vol., i, 368).

C. F. B.

Action of Magnesium Amalgam on Acetone. FRANÇOIS COUTURIER and LÉON MEUNIER (*Compt. rend.*, 1905, 140, 721—723. Compare Meunier, Abstr., 1902, i, 335).—Pure dry acetone (3 mols.) reacts energetically with magnesium amalgam (1 atom Mg) to form a

compound of acetone and magnesium, probably $\text{Mg} \begin{smallmatrix} \text{O}\cdot\text{CMe}_2 \\ | \\ \text{O}\cdot\text{CMe}_2 \end{smallmatrix}$, with 1 mol.

of acetone of crystallisation, from which pinacone hydrate is obtained by the action of water. Attempts to prepare tetramethylethylene oxide, $\text{O} \begin{smallmatrix} \text{CMe}_2 \\ | \\ \text{CMe}_2 \end{smallmatrix}$, by the dry distillation of the compound of acetone

and magnesium in a current of carbon dioxide at 250—300° were unsuccessful; the liquid distillate consisted of pinacolone with small quantities of acetone, isopropyl alcohol, and mesityl oxide. The author recommends this method of preparing pinacolone, as the yield (21 per cent. of the acetone) is far superior to that obtained by the ordinary process, starting from pinacone. M. A. W.

Mechanism of the Chlorination of Mixtures of Ketones and Water in presence of Marble. ANDRÉ KLING (*Bull. Soc. chim.*, 1905, [iii], 33, 322—324).—When a slow current of chlorine is passed into a mixture of acetone and water in presence of marble (Fritsch, *Abstr.*, 1893, i, 303; 1894, i, 490), the liquid becomes yellow; if the passage of chlorine is continued beyond this stage, an explosion may take place, and if the action of the gas is discontinued, the yellow colour disappears, slowly at the ordinary temperature and more rapidly on warming. By the application of Klimenko's method (*Abstr.*, 1904, ii, 205), the author has found that the yellow liquid first produced is essentially a solution of hypochlorous acid and has confirmed this by showing that acetone is chlorinated by a solution of hypochlorous acid. T. A. H.

Transformation of Sugars showing Multirotation. CHARLES TANRET (*Bull. Soc. chim.*, 1905, [iii], 33, 337—348. Compare *Abstr.*, 1895, i, 321, 490; Lowry, *Trans.*, 1899, 75, 213; Armstrong, *ibid.*, 1903, 83, 1305, and Behrend and Roth, *Abstr.*, 1904, i, 716).—The author agrees that the β -forms of dextrose, lactose, and galactose, which he regarded as existing in aqueous solutions of these sugars which had acquired constant rotatory powers, are merely equilibrium mixtures of the two other forms (now denominated the α - and β -sugars) first described by him (*loc. cit.*), and he suggests that these equilibrium mixtures might conveniently be called the s -forms.

When α -dextrose is heated at 100°, it is converted into the β -form, and a similar change slowly occurs at the ordinary temperature: thus a specimen of α -dextrose had $[\alpha]_D + 22.50^\circ$ in 1895 and in 1904 this had fallen to $+19.50^\circ$. Similar changes take place with the α -forms of lactose and galactose. Small quantities of cold water transform the β -forms of dextrose and galactose slowly, but completely, into the α -forms: the reverse change takes place when the α -forms are heated in aqueous solution.

The relative proportions of the α - and β -forms of dextrose, galactose, and lactose which constitute the equilibrium mixtures (s -forms) of these three sugars are remarkably similar, being 0.368 : 0.632, 0.354 : 0.646, and 0.376 : 0.624 respectively. T. A. H.

Anilides of Rhamnose and Arabinose. PETER HERMANN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 119—120).—Both rhamnose and arabinose readily react with aniline in alcoholic solutions.

Rhamnose anilide, $C_6H_{12}O_4 \cdot NPh$, separates from alcohol in slender, white, acicular crystals which begin to decompose at about 110° and melt at 121—127°; in alcoholic solution, $[\alpha]_D$ has the value -50.4° .

Arabinose anilide, $C_5H_{10}O_4 \cdot NPh$, separates from alcohol in slender, lemon-yellow crystals which begin to decompose at about 98° and melt at 103.5—106°. T. H. P.

Reversion of Artificial Starches. EUGÈNE ROUX (*Compt. rend.*, 1905, 140, 943—946. Compare this vol., i, 262).—Artificial starches formed from starch or amylocellulose form, on solution, a paste which suffers a similar reversion under the influence of water, acids, or alkalis to that which the paste from the natural product undergoes (compare Abstr., 1903, i, 679; 1904, i, 17, 227, 228, 294, 800), only the change is more rapid in the former than in the latter case. The product of the reversion in each case has the same properties as the original starch and only becomes soluble at the temperature at which the original starch was soluble; the reversion is therefore a return to the initial state (compare Maquenne, Abstr., 1904, i, 294). M. A. W.

Replacement of Hydrogen Atoms, attached to a Nitrogen Atom, by Methyl Groups, by means of Formaldehyde. WILHELM ESCHWEILER (*Ber.*, 1905, 38, 880—882. Compare D.R.-P. 80520, 1893).—The action of formaldehyde on ammonia, or on primary or secondary bases, or their salts, at 120—160°, results in the replacement of *N*-hydrogen atoms by methyl groups. At low temperatures, anhydro-derivatives are produced. With primary bases and with ammonia, the reaction takes place in two and three stages respectively. Hexamethylenetetramine yields as end-product in this reaction trimethylamine. G. Y.

Preparation of Trimethylamine by Methylation of Ammonia by means of Formaldehyde. ALBERT KOEPPEN (*Ber.*, 1905, 38, 882—884. Compare preceding abstract).—A yield of 70—80 grams of trimethylamine hydrochloride is obtained by heating 50 grams of ammonium chloride with 440 grams of 40 per cent. formaldehyde solution in an autoclave at 120°. The reaction is finished when the internal pressure has reached a maximum of 35—40 atmospheres. G. Y.

Compounds of Tervalent Cobalt with Ethylenediamine. LUDWIG GERB (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 43—79).—The author first discusses the ethylenediamine-cobalt compounds already described by Werner (Abstr., 1901, i, 510, 511, 512), Jörgensen, and others.

1:2-Dibromodiethylenediaminecobalt bromide, 1:2(CoEnBr₂)Br [En = ethylenediamine], separates from water in aggregates of black plates which, on crushing, yield a dark violet powder. When heated with concentrated hydrobromic acid, it is converted into the corresponding green 1:6-compound.

The action of sodium nitrite on 1:6-dichlorodiethylenediaminecobalt chloride yields: (1) the *flaveodiethylenediamine chloride*, [CoEn₂(NO₂)₂]Cl,

which crystallises in large, monoclinic plates; (2) the *roseoethylenediamine chloride*, [CoEn₂(NO₂)₂]Cl, which crystallises from dilute hydrochloric acid in thin plates; (3) (CoEnNO₂)NO₂, which forms pale yellow, cubical crystals, and (4) certain secondary products in very small quantities.

Chloronitritodiethylenediaminecobalt chloride, (CoEn₂Cl·ONO)Cl, separates from dilute hydrochloric acid in pale red, shining needles.

Chloronitritodiethylenediaminecobalt nitrate, $(\text{CoEn}_2\text{Cl}\cdot\text{ONO})\text{NO}_3$, is obtained as a pale red, crystalline precipitate.

Chloronitritodiethylenediaminecobalt sulphate, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)\text{HSO}_4$, forms a red, amorphous precipitate.

Chloronitritodiethylenediaminecobalt nitrite, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)\text{NO}_2$, forms a yellow precipitate.

Chloronitritodiethylenediaminecobalt iodide, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)\text{I}$, forms a red, microcrystalline precipitate soluble in water.

Chloronitritodiethylenediaminecobalt bromide, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)\text{Br}$, forms a red, crystalline precipitate soluble in water.

Chloronitritodiethylenediaminecobalt thiocyanate, $(\text{CoEn}_2\text{Cl}\cdot\text{NO}_2)\text{SCN}$, is obtained as a red, crystalline precipitate soluble in water.

Nitritothiocyano-diethylenediaminecobalt chloride,
 $[\text{CoEn}_2(\text{SCN})\cdot\text{NO}_2]\text{Cl} + 2\text{H}_2\text{O}$,

forms deep yellow needles, or pale yellow leaflets, which do not effloresce in the air.

Thiocyanonitritodiethylenediaminecobalt iodide, $[\text{CoEn}_2(\text{SCN})\cdot\text{NO}_2]\text{I}$, forms dark red, flat prisms soluble in water on prolonged boiling.

Thiocyanonitritodiethylenediaminecobalt nitrate,
 $[\text{CoEn}_2(\text{SCN})\cdot\text{NO}_2]\text{NO}_3$,

forms shining, badly developed plates soluble in water on prolonged boiling.

Thiocyanonitritodiethylenediaminecobalt bromide,
 $[\text{CoEn}_2(\text{SCN})\cdot\text{NO}_2]\text{Br}$,

forms small, drusy masses of a reddish-brown colour, readily soluble in water.

Thiocyanonitritodiethylenediaminecobalt thiocyanate,
 $[\text{CoEn}_2(\text{SCN})\cdot\text{NO}_2]\text{SCN}$,

forms large, yellowish-brown crystals soluble in water on long boiling. In acid solution, it gives, with potassium aurichloride, the compound $[\text{CoEn}_2(\text{SCN})\cdot\text{NO}_2]\text{AuCl}_2$.

Nitritonitratodiethylenediaminecobalt nitrate, $[\text{CoEn}_2(\text{NO}_2)\cdot\text{NO}_3]\text{NO}_3$, forms a pale yellow, crystalline precipitate, and the corresponding *nitrite* slender, yellow crystals.

T. H. P.

Characterisation of Lactones by means of Hydrazine.

EDMOND E. BLAISE and A. LUTTRINGER (*Compt. rend.*, 1905, 140, 790—792).—When lactones are heated on the water-bath with a slight excess of hydrazine hydrate until the water has been expelled, additive compounds, termed hydrazinolactones, are formed. These are very soluble in water and in alcohol, are nearly insoluble in ether, but can be easily crystallised from ethyl acetate solution. The chemical properties of the hydrazinolactones indicate that they are lactone additive compounds of the type $\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{R} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH}\cdot\text{NH}_2 \end{smallmatrix}$, and not hydrazides of the corresponding alcohol acids. Dilute sulphuric acid precipitates hydrazine sulphate from the aqueous solutions, and, when these are shaken with benzaldehyde, benzylideneazine is obtained. The crystalline substances slowly liberate hydrazine at 200°. The following derivatives were prepared. *Hydrazino-γ-methyl-*

butyrolactone, $\begin{matrix} \text{CHMe}\cdot\text{O} \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{matrix} > \text{C}(\text{OH})\cdot\text{NH}\cdot\text{NH}_2$, melts at 61—62°; *hydrazino- α -dimethylbutyrolactone* melts at 115°; *hydrazino- β - γ -dimethylbutyrolactone* melts at 96—97°; *hydrazino- α -methyl- γ -ethylbutyrolactone* melts at 124°, and *hydrazino- α -methyl- γ -n-amylobutyrolactone* melts at 116°. The method is also applicable to δ -lactones, but it is advisable to treat the lactone two or three times with hydrazine hydrate. *Hydrazino- α -methyl- δ -n-butylvalerolactone* was prepared; it melts at 76°.

H. M. D.

Cyanuric Acid Derivatives. ARTHUR HANTZSCH and HUGO BAUER (*Ber.*, 1905, **38**, 1005—1013; compare this vol., i, 317).—The cyanilic acid described by Liebig is identical with cyanuric acid.

Isomeric esters of cyanuric acid are described. Methyl cyanurate, $\text{C}_3\text{N}_3(\text{OMe})_3$, is prepared pure from cyanuric bromide and sodium methoxide; when cyanogen bromide is used instead of cyanuric bromide, mixtures of oily by-products are produced. Methyl cyanurate is readily hydrolysed by mineral acids at 100°. *Trimethyl $\frac{2}{3}$ - ψ -cyanurate*, $\text{N} \begin{matrix} \text{CO} - \text{NMe} \\ \diagup \quad \diagdown \\ \text{C}(\text{OMe}) \cdot \text{N} \end{matrix} > \text{C} \cdot \text{OMe}$, is formed in small yield by careful alkylation with methyl iodide of silver cyanate at -5° , polymerisation occurring between 2 mols. of the true methyl cyanate and 1 mol. of the methyl ψ -cyanate. It melts at 105° and is distinguished from the other methyl cyanurates described in being volatile with steam and in subliming without undergoing decomposition. When heated in a sealed tube with hydrochloric acid, it is hydrolysed with the formation of *N*-monomethyl cyanurate, melting at 282° (Fischer gives 284—286° uncorr.) and forming a characteristic copper salt.

Trimethyl $\frac{2}{3}$ - ψ -cyanurate, $\text{N} \begin{matrix} \text{CO} - \text{NMe} \\ \diagup \quad \diagdown \\ \text{C}(\text{OMe}) \cdot \text{NMe} \end{matrix} > \text{CO}$, is the main product of the action of trisilver cyanurate on methyl iodide at -10° , whilst trimethyl ψ -cyanurate is produced at higher temperatures. Trimethyl $\frac{2}{3}$ - ψ -cyanurate melts at 118° and, when heated at 180°, is converted into trimethyl ψ -cyanurate, melting at 170°. When heated at 100° with concentrated hydrochloric acid, it undergoes hydrolysis to *N*-dimethyl cyanurate melting at 222°. Trimethyl ψ -cyanurate was also prepared.

Tribenzyl ψ -cyanurate, prepared from benzyl iodide and silver cyanate, melts at 165°; its *hydrochloride* melts and decomposes at 128°.

Ethyl tricyanotricarboxylate, $\text{C}_3\text{N}_3(\text{CO}_2\text{Et})_3$, is trimolecular according to a determination of its molecular weight in chloroform. The free acid could not, however, be obtained from it owing to the ease with which decomposition occurs during hydrolysis.

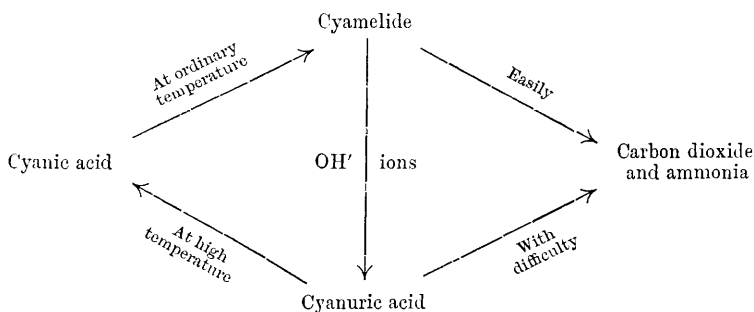
[With FRIEDRICH HOFMANN.]—*Tricyanocarbamide (cyanuric acid ureide)*, $\text{C}_3\text{N}_3(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_3$, prepared by heating carbamide first at 130° and then gradually allowing the temperature to rise to about 200°, is freed from the cyanuric acid formed by removing the latter with water; it is an amorphous powder, and sublimes with decomposition at an elevated temperature. It differs from cyamelide in being soluble without decomposition in much boiling water. It

exhibits both acid and basic properties and is soluble in dilute alkalis. Its *trisodium* salt, $C_6H_6O_3N_9Na_3 \cdot 5H_2O$, crystallises in tiny needles. The acid character of tricyanocarbamide is more marked than its basic character, since the substance separates unchanged from its solutions in dilute mineral acids.

Tricyanocarbamide is also formed by the following methods: by heating a mixture of cyanogen bromide and carbamide for 3 hours at 150° or in a sealed tube; by heating a mixture of cyanuric acid and carbamide at 180 – 190° , and by heating biuret. A. McK.

Cyanuric Acid Derivatives. OTTO DIELS (*Ber.*, 1905, 38, 1186–1188).—A criticism of certain statements made by Hantzsch and Bauer (preceding abstract). A. McK.

Cyamelide. ARTHUR HANTZSCH (*Ber.*, 1905, 38, 1013–1021).—Cyamelide is not produced together with cyanuric acid when carbamide is heated; tricyanocarbamide, which resembles cyamelide superficially, is, however, formed (compare preceding abstracts). The molecular weight of cyamelide, owing to the insolubility of the compound in the ordinary solvents, has not been determined directly. By indirect methods, it is shown that cyamelide is isomeric with cyanuric acid. Its formation from cyanic acid is a trimolecular reaction. Cyamelide is more readily decomposed than is cyanuric acid; by the action of sulphuric acid on the two isomerides, carbon dioxide and ammonia are formed at a lower temperature from cyamelide than from cyanuric acid. Cyamelide is more labile than cyanuric acid; it is accordingly the main product of the polymerisation of cyanic acid. That in many reactions cyamelide appears to be more stable than cyanuric acid is due to the latter being a *pseudo*-acid, which is convertible into the more reactive true acid. The relationships between cyanic acid, cyamelide, and cyanuric acid are expressed as follows:



Cyamelide is not a stereoisomeride of cyanuric acid or of *pseudo*-cyanuric acid. It cannot be regarded as a tricyanogen derivative; it cannot contain the group $\cdot N:C(OH)$ or the group $\cdot NH \cdot CO$, since it is neither a true acid nor a *pseudo*-acid.

Cyamelide is a polymeric form of ψ -cyanic acid, and is represented by the formula $NH:C \begin{matrix} \diagup O \cdot C(:NH) \\ \diagdown O \cdot C(:NH) \end{matrix} > O$.

[With FRIEDRICH HOFMANN and M. LEHMANN.]—Oxalic acid and potassium cyanate were mixed at the ordinary temperature until the product, which was at first semi-liquid, solidified and until the odour of cyanic acid was no longer evident. On the addition of water, cyamelide was obtained as a white mass. Cyamelide is slightly soluble in water and in concentrated sulphuric acid. It is not acted on by phosphorus haloids, acetyl chloride, acetic anhydride, chlorine, or bromine. By the action of a 20 per cent. aqueous solution of sodium hydroxide, it is converted into trisodium cyanurate.

Monomeric cyamelide, $(C_3O_3N_3)_2H_4Hg, 3H_2O$, prepared by the action of freshly-prepared cyamelide on freshly-precipitated mercuric oxide in aqueous suspension, is insoluble in indifferent media and in ammonia, pyridine, dilute acids, and dilute alkali hydroxides. By the action of hydrogen sulphide or of alkali sulphides, mercuric sulphide is formed together with cyamelide. When heated at 180° , it is decomposed according to the equation: $3(C_3H_2O_3N_3)_2Hg, 3H_2O = 3H_2O + (C_3O_3N_3)_2Hg_3 + 12HCON$.
A. McK.

Transformations of Amides of α -Haloid Acids under the Action of Bromine and Alkali Hydroxide. NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 103—105).—The treatment of α -bromoisobutyric acid with bromine and potassium hydroxide, followed by distillation, yields: (1) β -dibromopropane and (2) a strongly alkaline liquid, which, when acidified with hydrochloric acid and distilled, gives 54 per cent. of the theoretical quantity of acetone.
T. H. P.

Action of Hypochlorites on Carbamide: New Synthesis of Hydrazine. PETR J. SCHESTAKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1—7).—The action of sodium hypochlorite on carbamide in alkaline solution proceeds in the following five stages:

1. $NH_2 \cdot CO \cdot NH_2 + NaOCl = NH_2 \cdot C(ONa) \cdot NCl + H_2O$.
2. $NH_2 \cdot C(ONa) \cdot NCl = NH_2 \cdot N \cdot CCl \cdot ONa$.
3. $NH_2 \cdot N \cdot CCl \cdot ONa + NaOH = NH_2 \cdot NH \cdot CO_2Na + NaCl$.
4. $NH_2 \cdot NH \cdot CO_2Na + H_2O = NH_2 \cdot NH_2 + NaHCO_3$.
5. $NH_2 \cdot NH_2 + 2NaOCl = N_2 + 2H_2O + 2NaCl$.

The last phase only occurs when excess of the hypochlorite is used and it is more probable that it is not the hydrazine which undergoes decomposition but the sodium hydrazinecarboxylate.
T. H. P.

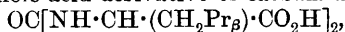
Carbamide Derivatives of Natural (*l*) Leucine. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1905, **140**, 859—861. Compare this vol., i, 178).—When one molecule of the ethyl ester of α -carbiminoisohexoxic acid, $CO \cdot N \cdot CH \cdot (CH_2Pr^B) \cdot CO_2Et$, reacts with one molecule of ammonia in aqueous solution, the ethyl ester of isobutylhydantoic acid is obtained. When this is saponified and the solution acidified with mineral acid, the free acid,

$NH_2 \cdot CO \cdot NH \cdot CH \cdot (CH_2Pr^B) \cdot CO_2H$, separates. It melts at 200° and is identical with the substance obtained by the action of leucine on carbamide (*loc. cit.*).

When aniline is substituted for ammonia in the above reaction, the acid, $NHPh \cdot CO \cdot NH \cdot CH(CH_2Pr^B) \cdot CO_2H$, is obtained. It crystallises

in slender needles, melts at 115° , and is only slightly soluble in cold water, but more readily soluble in hot water, in alcohol, or ether.

When ethyl α -carbiminoisohexoate (1 mol.) is gradually added to a cooled alkaline solution of *l*-leucine (1 mol.), it slowly passes into solution; after saponification and addition of a mineral acid, the symmetrical α -isohexoic acid derivative of carbamide,



is precipitated. It crystallises with difficulty, dissolves only slightly in cold water, more readily in hot. It is soluble in ether and benzene and very soluble in alcohol. Its alkali and copper salts are soluble, the lead and silver salts insoluble.

H. M. D.

Oxidation of Pyrrole to Maleimide. GIUSEPPE PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 214—216).—The maleimide prepared by the oxidation of pyrrole (see Plancher and Cattadori, *Abstr.*, 1904, i, 770) crystallises in the triclinic system [G. Boeris gives: $a:b:c = 1.0686:1:0.8648$; $\alpha = 90^{\circ}15'$, $\beta = 105^{\circ}7'$, $\gamma = 108^{\circ}53'$]. It is not identical with the isomeric fumarimide obtained from ammonium malate, and when boiled with sodium hydroxide solution yields ammonia and maleic acid. With phenylhydrazine, it yields *maleamide-phenylhydrazide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, which separates from alcohol in pale yellow crystals melting at 147 — 148° ; the *amide anilide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{NHPh}$, is deposited from benzene in pale yellow crystals melting at 173 — 175° .

T. H. P.

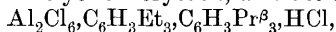
New General Methods of Hydrogenation and of Molecular Reactions based on the use of Finely Divided Metals. I. PAUL SABATIER and JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1905, [viii], 4, 319—432).—The experimental results described in this paper have already been published (compare *Abstr.*, 1900, i, 421, 469, 470, 471, 534; 1901, i, 195, 263, 459, 638; 1902, i, 333, 525, 581, 701; ii, 317, 605; 1903, i, 393, 453, 454, 686, 733; 1904, i, 156, 303, 305, 660; this vol., i, 254; compare also Brunel, *Abstr.*, 1904, i, 158). For a detailed description of the method of employing this new process of hydrogenation, the original must be consulted; the activity of the metal, or catalyst, in this process like that of a living ferment, exhibits three distinct phases: the initial phase, usually of short duration, corresponds with the superficial modification of the metal due to the replacement of the atmosphere of hydrogen by one of the vaporised compound; the second or normal phase is usually of long duration, in the case of the hydrogenation of benzene to cyclohexane the same quantity of nickel was used almost continuously for over a month; whilst the third phase corresponds with the decay in the activity of the metal due to a change in its surface, brought about by traces of the halogen elements, or of sulphur, or by a decomposition of carbonaceous or tarry matter, especially if the hydrogenation has been conducted at a high temperature.

Eijkman (compare *Chemisch Weekblad*, I. 7; *Chem. Centr.*, 1903, [ii], 989) has employed the method of hydrogenation described in this paper to convert hydrindene into dicyclononane boiling at 163° ;

diphenylmethane into dicyclohexylmethane boiling at 251° ; diphenyl into phenylcyclohexane boiling at 238° under 770 mm. pressure and crystallising at 0° ; cyclopentadiene into pentamethylene boiling at 49° ; and dicyclopentadiene into tricyclodecane boiling at 193° , melting at 77° , and having an odour of camphor. M. A. W.

Combination of Hydrocarbons or of Hydrogen Chloride with Compounds of Aluminium Chloride which act as Ferments.

GABRIEL GUSTAVSON (*Compt. rend.*, 1905, **140**, 940—941. Compare Abstr., 1903, i, 470, 804).—When aluminium chloride is added to a mixture of benzene and isopropyl chloride at a low temperature, the compound $\text{Al}_2\text{Cl}_6 \cdot 2\text{C}_6\text{H}_3\text{Pr}^{\beta}_3 \cdot \text{HCl}$ is obtained in the form of yellow crystals which are decomposed by water yielding triisopropylbenzene, and melt and decompose at 50° forming triisopropylbenzene, hydrogen chloride, and the compound $\text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_3\text{Pr}^{\beta}_3$; this acts as a ferment, combining with benzene to form the compound $\text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_3\text{Pr}^{\beta}_3 \cdot 6\text{C}_6\text{H}_6$, which reacts with isopropyl chloride to form the yellow, crystalline substance described above. The compound $\text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_3\text{Et}_3 \cdot \text{HCl}$, obtained by the action of hydrogen chloride on $\text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_3\text{Et}_3$ and $\text{C}_6\text{H}_3\text{Et}_3$ at -10° , forms yellow crystals, and the compound



similarly prepared, is also yellow.

Triisopropylbenzene, prepared as above, boils at 234 — 236° and the magnesium salt of its sulphonic derivative, $(\text{C}_6\text{H}_2\text{Pr}^{\beta}_3\text{SO}_3)_2\text{Mg} \cdot 7\text{H}_2\text{O}$, is very sparingly soluble, one part of the salt dissolving in 1414 parts of water at 19° . M. A. W.

Monochloro-derivatives of Methylcyclohexane. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, **140**, 840—843. Compare Abstr., 1903, i, 686).—When methylcyclohexane is treated with chlorine at the ordinary temperature together with other products, a mixture of monochloro-substitution products is obtained. To ascertain the nature of these, the authors have prepared the five possible chloromethylcyclohexanes by action of phosphorus pentachloride on the corresponding hydroxy-compounds.

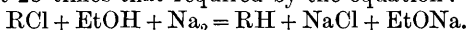
Hexahydrobenzyl chloride, $\text{C}_6\text{H}_{11} \cdot \text{CH}_2\text{Cl}$, is a colourless liquid of sp. gr. 1.0038 at $0^{\circ}/0^{\circ}$, which boils at 166° (corr.) under 760 mm. without sensible decomposition. 2-Chloromethylcyclohexane has a sp. gr. 1.001 at $0^{\circ}/0^{\circ}$ and boils at 156° with slight decomposition; 3-chloromethylcyclohexane has a sp. gr. 1.011 at $0^{\circ}/0^{\circ}$ and boils at 157° with slight decomposition; 4-chloromethylcyclohexane has a sp. gr. 0.992 at $0^{\circ}/0^{\circ}$ and boils at 158° , decomposing appreciably. 1-Chloromethylcyclohexane has a sp. gr. 0.996 at $0^{\circ}/0^{\circ}$ and boils at 148 — 151° with considerable decomposition. From these data, it is concluded that the product of chlorination of methylcyclohexane contains neither hexahydrobenzyl chloride nor 1-chloromethylcyclohexane.

In the further investigation of the nature of the product of chlorination, this was converted by Grignard's method into magnesium methylcyclohexyl chloride, which on prolonged oxidation in a current of pure dry oxygen and treatment with cold water gives the alcohols corresponding to the chloro-derivatives.

From the results so obtained, it is considered that the monochloro-derivatives formed by direct chlorination of methylcyclohexane consist of about 40 per cent. of 2-chloromethylcyclohexane and about 60 per cent. of the 3-derivative associated with a little 4-chloromethylcyclohexane.

H. M. D.

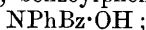
Removal of Halogens from the Benzene Nucleus by the Action of Sodium and Ethyl Alcohol. A. STEPANOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 12—16).—In order to remove the halogen contained in the benzene nucleus of an aromatic compound, the author takes a definite weight of the latter and heats on a water-bath in a reflux apparatus with 20—40 c.c. of 98 per cent. alcohol, sodium being dropped in small pieces down the condenser tube until the total amount added is about 25 times that required by the equation :



When the sodium is all dissolved, from 20 to 40 c.c. of water are added and the alcohol then distilled off. On cooling, the contents of the flask are strongly acidified by the addition of dilute nitric acid and the halogen determined by titration according to Volhard's method. When treated in this way, chlorobenzene, hexachlorobenzene, bromobenzene, *p*-chlorotoluene, and bromonaphthalene give up the whole of the halogen they contain. The method may hence be used as a means of estimating the halogen in these compounds.

T. H. P.

Chemical Action caused by Light. VIII. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1905, **38**, 1176—1184).—When a mixture of benzaldehyde and nitrobenzene is exposed to light for several months, the following substances are formed: benzoic acid, dibenzoylphenylhydroxylamine, $\text{NPhBz}\cdot\text{OBz}$; benzoylphenylhydroxylamine,



dibenzoyl-*p*-aminophenol; *o*-benzoylaminophenol, benzanilide, azoxybenzene, and *o*-hydroxyazobenzene. The proportion of the last two substances is increased by increasing the time of exposure to light; they are formed at the expense of the benzoylphenylhydroxylamine and *o*-benzoylaminophenol. A theory of the mechanism of the interaction is given, based on Bamberger's experiments on the decomposition of nitrosobenzene (*Abstr.*, 1900, i, 531, and 1902, i, 505). W. A. D.

Uses of Metallic Calcium. ERNST BECKMANN [with KARL BECK and HANS SCHLEGEL] (*Ber.*, 1905, **38**, 904—906).—Nitrobenzene is reduced by calcium in alcoholic solution, in presence of mercuric chloride or copper sulphate, to azoxybenzene, or in alcoholic hydrochloric acid solution to aniline. Benzenesulphonic chloride is reduced by calcium in alkaline solution to the sulphinic acid, but in acid solution to thiophenol; whilst oximes are reduced in either solution to amines.

When boiled with iodobenzene in absolute ethereal solution containing traces of iodine, calcium forms *calcium phenyl iodide*, which is obtained as a brown powder and is moderately soluble in ether. When treated with carbon dioxide and water, successively, it yields benzoic acid; with benzaldehyde and water, it forms benzhydrol.

Calcium and ethyl iodide do not react when boiled in benzene, but in ethereal solution an *additive* compound of ether and calcium ethyl iodide, $\text{OEt}_2 \cdot \text{CaEtI}$, is formed as an odourless, white substance which is stable on exposure to air, but decomposes at 40° , and when treated with water yields ethane.

Metallic oxides and sulphides may be reduced to the metals by calcium instead of aluminium, by Goldschmidt's method (Abstr., 1898, ii, 509). G. Y.

Amides, Nitriles, and Thioamides of Arylsulphonacetic Acids.

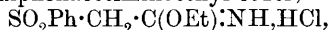
JULIUS TRÖGER and WALDEMAR HILLE (*J. pr. Chem.*, 1905, [ii], 71, 201—235. Compare Otto, Abstr., 1885, 535).—Arylsulphonacetamides are formed by the action of chloroacetamide on sodium arylsulphonates in boiling alcohol solution or, when moistened with alcohol, in a sealed tube at 100° . Benzenesulphonacetamide, $\text{SO}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$, crystallises in glistening, white needles and melts at 156° (m. p. 153° , Otto, *loc. cit.*). *p*-Toluenesulphonacetamide crystallises in slender, white needles, melts at 166° , and dissolves easily in alcohol or ethyl acetate. *o*-Toluenesulphonacetamide crystallises in slender, white needles and melts at 144° .

To prepare *m*-toluenesulphinic acid by Gattermann's method, *m*-toluidine is diazotised in dilute solution, in presence of a large excess of acid; the treatment with sulphur dioxide must not be too prolonged, and the copper powder must be added before the appearance of the red precipitate (Abstr., 1904, i, 118). *m*-Toluenesulphinic acid is an unstable oil, which is only slightly soluble in cold ether; the sodium and barium salts were prepared. *m*-Toluenesulphonacetamide crystallises in slender, white needles and melts at 146° . 1:3-Xylene-4-sulphonacetamide crystallises in soft needles and melts at 149° . *p*-Chlorobenzenesulphonacetamide crystallises in long, glistening needles and melts at 169° . *p*-Bromobenzenesulphonacetamide crystallises in stout, white needles and melts at 166° . *p*-Iodobenzenesulphonacetamide forms small, white crystals and melts at 189° . α -Naphthalenesulphonacetamide forms a yellow, crystalline powder and melts at 162° . β -Naphthalenesulphonacetamide separates from alcohol as a white, crystalline powder and melts at 194° .

The action of bromine on benzenesulphonacetamide in glacial acetic acid solution leads to the formation of *benzenesulphonbromoacetobromamide*, $\text{SO}_2\text{Ph} \cdot \text{CH} \cdot \text{Br} \cdot \text{CO} \cdot \text{NH} \cdot \text{Br}$, which crystallises in glistening, white leaflets, melts at 139° , dissolves readily in hot alcohol, and liberates iodine from potassium iodide in acid solution, and when acted on by 3 mols. of potassium hydroxide in 30 per cent. warm aqueous solution or by sodium ethoxide, yields phenyldibromomethylsulphone, $\text{CHBr}_2 \cdot \text{SO}_2\text{Ph}$. Phenyltribromomethylsulphone, $\text{CBr}_3 \cdot \text{SO}_2\text{Ph}$, is formed by the action of bromine and aqueous sodium hydroxide on benzenesulphonacetamide or on phenyldibromomethylsulphone; it crystallises in glistening, white needles and melts at 145° . The action of chlorine on benzenesulphonacetamide in glacial acetic acid solution leads to the formation of *benzenesulphondichloroacetochloroamide*, $\text{SO}_2\text{Ph} \cdot \text{CCl}_2 \cdot \text{CO} \cdot \text{NHCl}$, which crystallises in thick, white, glistening needles, melts at 144° , and when treated with 30 per cent. potassium

hydroxide solution yields a *product*, which is probably phenyltrichloromethylsulphone. *p-Toluenesulphonacetobromoamide*, formed by the action of 1 mol. of bromine on *p*-toluenesulphonacetamide, crystallises in white needles and melts at 177°. With an excess of bromine, *p-toluenesulphobromoacetobromoamide* is obtained, crystallising in prisms, melting at 138°, and when warmed with aqueous potassium hydroxide yielding *p*-tolylidibromomethylsulphone, which is also formed by the action of bromine and aqueous sodium hydroxide on *p*-toluenesulphonacetamide. *p-Toluenesulphonchloroacetochloroamide*, obtained by the action of chlorine on *p*-toluenesulphonacetamide, forms white crystals, melts at 124°, and when treated with aqueous sodium hydroxide yields an oily *product*. β -Naphthalenesulphondibromoacetobromoamide forms a white, crystalline powder, melts at 172—174°, and is converted by aqueous potassium hydroxide into β -naphthylidibromomethylsulphone, which melts at 108—112°; impure β -naphthyltribromomethylsulphone, melting at 150—160°, is obtained by the action of bromine and aqueous sodium hydroxide on β -naphthalenesulphonacetamide. The action of chlorine on β -naphthalenesulphonacetamide leads to the formation of an impure *tetrachloro*-derivative melting at 94°.

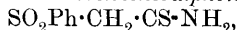
Arylsulphonacetonitriles are formed by the action of chloroacetonitrile on sodium arylsulphonates. *Benzenesulphonacetonitrile*, $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CN}$, crystallises in glistening, white needles, melts at 114°, and is moderately soluble in alcohol, but only slightly so in water. When treated with alcohol and hydrogen chloride, in ethereal solution, it yields the *hydrochloride* of benzenesulphonacetiminoethyl ether,



which forms small, white crystals. *p-Toluenesulphonacetonitrile* forms white, refractive crystals and melts at 145—146°. *o-Toluenesulphonacetonitrile* is obtained as an oil, which gradually solidifies to a crystalline mass. *m-Toluenesulphonacetonitrile* crystallises in needles and melts at 168°. 1 : 3-*Xylene-4-sulphonacetonitrile* crystallises in white needles and melts at 79—80°. α -Naphthalenesulphonacetonitrile crystallises in long needles and melts at 109°. β -Naphthalenesulphonacetonitrile forms small crystals and melts at 95°. *p*-Chlorobenzenesulphinic acid is prepared by Gattermann's method from *p*-chloroaniline; from *p*-chlorobenzenesulphonic chloride, by Otto and Schiller's method; and from sodium *p*-chlorobenzenethiosulphonate by the action of mineral acids or of aqueous potassium cyanide solution. *p-Chlorobenzenesulphonacetonitrile* forms glistening, white crystals and melts at 169°. *p-Bromobenzenesulphonacetonitrile* forms small, glistening crystals and melts at 194°. *p-Iodobenzenesulphonacetonitrile* is crystalline and melts at 213—214°. *m-Phenylenedisulphonacetonitrile*, $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{CH}_2\cdot\text{CN})_2$, is crystalline and melts at 164°. 1 : 2 : 4-*Tolylendisulphonacetonitrile* crystallises in small needles and melts at 179°. With sodium in absolute alcoholic solution, or with cold dilute aqueous sodium hydroxide, arylsulphonacetonitriles form *monosodium* and *disodium* derivatives, which are soluble in water and are decomposed by a current of carbon dioxide. When treated with reducing agents, arylsulphonacetonitriles remain unchanged, or are decomposed to sulphinic acids.

Arylsulphonthioacetamides are formed by the action of hydrogen sulphide on arylsulphonacetonitriles in presence of alcoholic ammonia

at the ordinary temperature. *Benzenesulphonthioacetamide*,



forms yellow crystals, melts at 170° , and forms a sodium derivative, which is soluble in water and is decomposed by carbon dioxide. It is reduced by alcoholic hydrochloric acid and zinc dust to hydrogen sulphide and phenyl mercaptan, which is oxidised by the oxygen of the air to phenyl disulphide; by aluminium in alkaline solution to phenyl-mercaptan and ammonia. *p-Toluenesulphonthioacetamide* crystallises in long, yellow needles and melts at 179° . *m-Toluenesulphonthioacetamide* forms a white, crystalline powder and melts at 142° . *1:3-Xylene-4-sulphonthioacetamide* forms small, yellow crystals and melts at 118° . *α -Naphthalenesulphonthioacetamide* forms small, yellow crystals and melts at 204° . *β -Naphthalenesulphonthioacetamide* forms small, yellow crystals and melts and decomposes at 170° . *p-Chlorobenzene-sulphonthioacetamide* melts at 181° . *p-Bromobenzene-sulphonthioacetamide* forms small, glistening, yellow crystals and melts at 207° . *p-Iodobenzene-sulphonthioacetamide* forms a yellow, crystalline powder and melts at 203° . *m-Phenylenedisulphonthioacetamide*, $\text{C}_6\text{H}_4(\text{SO}_2\cdot\text{CH}_2\cdot\text{CS}\cdot\text{NH}_2)_2$, forms a grey powder and melts at 189° . G. Y.

Hydrides of Phenanthrene. PIERRE BRETEAU (*Compt. rend.*, 1905, **140**, 942—943. Compare Graebe, *Abstr.*, 1873, 896; Bamberger and Lodter, *Abstr.*, 1888, 292; Liebermann and Spiegel, *Abstr.*, 1889, 719).—When phenanthrene is directly hydrogenated in the presence of reduced nickel at 200° by Sabatier and Senderens' method, a mixture of hexahydro- and octahydro-phenanthrene is obtained which can be separated by fractional distillation.

Hexahydrophenanthrene, $\text{C}_{14}\text{H}_{16}$, is a pale yellow liquid, boiling at $305\text{--}307^\circ$ under 760 mm. or at $165\text{--}167^\circ$ under 13 mm. pressure; it melts at -3° , has a sp. gr. 1.053 at 0° or 1.043 at 15° , and n_D 1.580 at 15° ; is soluble in alcohol, acetic acid, ether, benzene, or chloroform; forms a *picrate* melting at 106° and two solid bromine derivatives melting at 150° and 142° respectively; it is readily oxidised by dilute nitric acid, potassium permanganate, or chromic acid, but does not yield phenanthraquinone. *Octahydrophenanthrene*, $\text{C}_{14}\text{H}_{18}$ (compare Graebe, *Abstr.*, 1873, 896), is a colourless liquid boiling at $280\text{--}285^\circ$ under 760 mm., or at $123\text{--}124^\circ$ under 13 mm. pressure; it has a sp. gr. 1.006 at 0° , or 0.993 at 15° , n_D 1.537 at 15° ; is slightly soluble in cold, more readily so in hot alcohol, very soluble in ether, benzene, or chloroform; it does not form a solid *picrate*, it yields unstable liquid bromine derivatives, and behaves towards oxidising agents in the same way as the hexahydro-compound.

M. A. W.

Separation of Primary and Secondary Amines. OSCAR HINSBERG and J. KESSLER (*Ber.*, 1905, **38**, 906—911. Compare *Abstr.*, 1891, 49; Solonina, *Abstr.*, 1900, i, 147).—Dibenzene-sulphonamides, $\text{NR}(\text{SO}_2\text{Ph})_2$, formed from primary amines, are converted into benzenesulphonamides, $\text{NHR}\cdot\text{SO}_2\text{Ph}$, when warmed with sodium ethoxide in alcoholic solution. Benzenesulphonamides derived from primary aliphatic or hydrocyclic amines, containing more than

6 carbon atoms, are insoluble in aqueous alkali hydroxides, and react with sodium in ethereal solution to form sodium derivatives, which are insoluble in ether. Benzenesulphonamides derived from secondary amines are soluble in ether and are not acted on by sodium. Hinsberg's method for the separation of primary and secondary amines is modified accordingly.

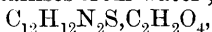
Dibenzenesulphonethylamide, $\text{NEt}(\text{SO}_2\text{Ph})_2$, crystallises in needles and melts at $81-82^\circ$. *Benzenesulphonheptadecylamide* crystallises in glistening needles and melts at $62-63^\circ$. *Benzenesulphon-o-xylidide* crystallises in colourless prisms and melts at 118° . *Dibenzenesulphon-o-xylidide* crystallises in needles and melts at 155° . *Dibenzenesulphon-p-xylidide* crystallises in needles and melts at $186-187^\circ$. *Benzenesulphon- ψ -cumidide* crystallises in glistening, colourless leaflets and melts at $136-137^\circ$. *Dibenzenesulphon- ψ -cumidide* crystallises in thin, white needles and melts at $186-187^\circ$.

Benzenesulphonethyl-p-xylidide, formed by heating benzenesulphon-p-xylidide with ethyl iodide and sodium ethoxide in alcoholic solution, crystallises in stellate groups of white needles, melts at 70° , and is hydrolysed by concentrated hydrochloric acid to *ethyl-p-xylidine*; this is a refractive oil, which has an odour resembling naphthalene, becomes dark on exposure to air, and boils at $222-223^\circ$ under 748 mm. pressure. *Tetrabenzenesulphon-m-phenylenediamide*, $\text{C}_6\text{H}_4[\text{N}(\text{SO}_2\text{Ph})_2]_2$, crystallises in glistening, silver leaflets and melts at 217° . *Tetrabenzenesulphon-p-phenylenediamide* crystallises in needles and melts at $235-236^\circ$. *Benzenesulphon-m-toluidide* forms a white, crystalline crust and melts at 80° . G. Y.

Action of Sulphur on Aniline and Aniline Hydrochloride. OSCAR HINSBERG (*Ber.*, 1905, **38**, 1130—1137. Compare Hofmann, *Abstr.*, 1895, i, 87).—The product obtained on fusing a mixture of aniline, aniline hydrochloride, and sulphur contains diphenylamine, dithioaniline, Merz and Weith's thioaniline, and a thioaniline which melts at 58° . Hofmann's thioaniline, melting at 85.5° , was probably a mixture.

Dithioaniline (diaminophenyl disulphide) crystallises in yellow prisms or slender needles, melts at $76-77^\circ$, is easily soluble in alcohol, benzene, or ether, and is reduced by zinc dust and hydrochloric acid to aminophenyl mercaptan. The hydrochloride forms a crystalline powder; the diacetyl derivative, $(\text{NHAc}\cdot\text{C}_6\text{H}_4)_2\text{S}_2$, crystallises in small needles, melts at 182° , and when boiled with zinc dust and aqueous sodium hydroxide dissolves, and on acidification yields a precipitate, which is probably acetylaminophenyl mercaptan.

Thioaniline (*op*-diaminophenyl sulphide) (Nietzki and Bothof, *Abstr.*, 1897, i, 36), which melts at 58° , crystallises in slender needles or stellate groups of glistening needles, is easily soluble in alcohol, ether, or benzene, and with lead peroxide in alcoholic hydrochloric acid solution gives a violet coloration. The *hydrochloride*, $\text{C}_{12}\text{H}_{12}\text{N}_2\text{S}_2\text{HCl}$, crystallises in thick prisms or stellate groups of needles; the *sulphate*, $(\text{C}_{12}\text{H}_{12}\text{N}_2\text{S})_2\cdot\text{H}_2\text{SO}_4$, crystallises from water; the *oxalate*,

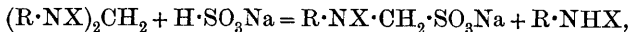


crystallises in nodular aggregates of needles. The *diacetyl* derivative,

$C_{16}H_{16}O_2N_2S$, crystallises in slender needles, and when heated with concentrated sulphuric acid yields a product which is soluble in aqueous alkali hydroxide. G. Y.

Phenylcarbimide as a Reagent for determining the Constitution of Tautomeric Compounds. HEINRICH GOLDSCHMIDT (*Ber.*, 1905, 38, 1096—1098).—A reply to Michael (this vol., i, 195). G. Y.

ω -Sulphomethyl Derivatives of Aromatic Amines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 156760).—Diphenamine compounds, prepared by the combination of formaldehyde (1 mol.) with an aromatic amine (2 mols.) (Eberhardt and Welter, *Abstr.*, 1894, i, 451; Eibner, *Abstr.*, 1899, i, 41), react with sodium hydrogen sulphite to form ω -sulphomethyl derivatives of the amines, according to the equation:



where R = aryl, X = hydrogen or alkyl. The products are identical with those obtained from methylenedianiline and its derivatives (*Abstr.*, 1903, i, 336).

Sodium ω -sulphomethyl-p-toluidine, $C_6H_4Me \cdot NH \cdot CH_2 \cdot SO_3Na$, from methylenedi-p-toluidine, forms glistening, white leaflets.

The *sodium salt of ω -sulphomethylethylaniline*, from the methylene compound, $CH_2(C_6H_5Et)_2$, crystallises in glistening leaflets. Potassium cyanide forms *ω -cyanomethylethylaniline*, a colourless oil, converted by concentrated sulphuric acid into the *amide*, melting at 114—115°. Ammonium sulphide forms the *thioamide* melting at 140°; hydroxylamine forms the *amidoxime*, melting at 72°.

Sodium hydrogen ω -sulphomethylanthranilate, from methylenedi-anthranilic acid, forms yellowish-white needles or leaflets.

C. H. D.

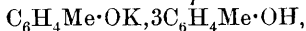
Action of Diphenylamine on Nitric Acid. ISIDORE BAY (*Compt. rend.*, 1905, 140, 796—797).—The intense blue coloration which diphenylamine sulphate gives with nitric acid is also obtained with a large number of other oxidising agents. Diphenylamine and other analogous aromatic amines are to be regarded as the leuco-bases of the coloured oxidation products. H. M. D.

New Additive Products of Tetrahydrobenzene. LÉON BRUNEL (*Bull. Soc. chim.*, 1905, [iii], 33, 382—384. Compare *Abstr.*, 1903, i, 157).—When cyclohexene, dissolved in ether, is treated with acid anhydrides in presence of mercuric oxide and iodine, esters of α -iodohydroxycyclohexane (*loc. cit.*) are formed. The *acetate*, $C_6H_{10}I \cdot OAc$, is an aromatic, faintly yellow liquid, has a sp. gr. 1.61 at 0°, and decomposes when distilled even under reduced pressure. The *propionate*, $C_2H_5 \cdot CO_2 \cdot C_6H_{10}I$, resembles the acetate and has a sp. gr. 1.54 at 0°.

This reaction is regarded as taking place in two stages, thus: $Ac_2O + HgO + I_2 + C_6H_{10} = C_6H_{10}I \cdot OAc + HgI \cdot OAc$ and $HgI \cdot OAc + I_2 + C_6H_{10} = C_6H_{10}I \cdot OAc + HgI_2$, and if insufficient iodine is used the intermediate mercury acetoiodide may be isolated. The mercuric salt of

the appropriate organic acid may be used in place of the acid anhydride. T. A. H.

Crystalline Double Compounds of Phenols with Alkali Phenoxides. CURT GENTSCH (D.R.-P. 156761 and 157616).—Phenols are known to dissolve in solutions of alkali phenoxides. It is found that crystalline double compounds may be prepared by adding dry alkali carbonate or hydroxide to a solution of the phenol in an indifferent solvent and boiling the mass with benzene or alcohol, from which the compound crystallises on cooling. The *compound* from phenol and potassium phenoxide, $C_6H_5 \cdot OK, 3C_6H_5 \cdot OH$, forms glistening needles and melts at 106—108°. The *p*-cresol *compound*,



melts at 146—147°, the corresponding *compound* from *m*-cresol melts at 88°. The ortho- and meta-compounds dissolve more readily in benzene than the para-compound, and the method may thus be used for the separation of the isomeric cresols. C. H. D.

2-Hydroxydibenzyl. STANISLAUS VON KOSTANECKI, A. ROST, and WLADISLAUS SZABRAŃSKI (*Ber.*, 1905, 38, 943—944).—2-Methoxydibenzyl, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH_2Ph$, obtained by reducing 2-methoxystilbene with sodium and alcohol, is a colourless oil distilling at 295°, and when heated with hydriodic acid yields 2-hydroxydibenzyl, which crystallises from dilute alcohol in colourless plates melting at 81°. Ethyl bromoacetate reacts with an alcoholic solution of the sodium derivative of 2-hydroxydibenzyl, yielding crude *ethyl 2-dibenzylglyoxylacetate*, $CH_2Ph \cdot CH_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2Et$, and this is readily hydrolysed to the *acid*, $C_{16}H_{16}O_3$, which crystallises from dilute alcohol in large, colourless needles melting at 137°. J. J. S.

Derivatives of the Pentamethylene Series. JULIUS VON BRAUN and ADOLPH STEINDORFF (*Ber.*, 1905, 38, 956—966. Compare Abstr., 1904, i, 731, 918).—*α*-Diphenoxypentane, $OPh \cdot [CH_2]_5 \cdot OPh$, obtained by the action of sodium phenoxide on *α*-dichloro-, dibromo- or di-iodo-pentane, forms colourless crystals, melts at 48—49°, and boils at 215—217° under 12 mm. and at about 340° under the ordinary pressure. It is best prepared from the crude *α*-dichloropentane obtained from the action of phosphorus pentachloride on benzoylpiperidine, containing much benzonitrile. When the diphenyl ether is heated with hydrobromic acid at 170°, it gives *α*-dibromopentane, whilst by using hydriodic acid, *α*-di-iodopentane, boiling at 135—136° under 12 mm. pressure, is obtained in nearly theoretical yield (compare Hamonet, Abstr., 1904, i, 643).

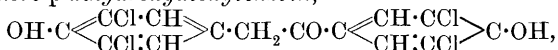
α-Chloro *ε*-phenoxypentane, $CH_2Cl \cdot [CH_2]_4 \cdot OPh$, prepared by converting benzoyl-*ε*-iodopentylamine, $NHBz \cdot [CH_2]_5 \cdot I$, into benzoyl-*ε*-phenoxypentylamine by means of sodium phenoxide and distilling the crude product with phosphorus pentachloride, boils at 155° under 15 mm. and at 283—285° under the ordinary pressure, undergoing in the latter case a slight decomposition; it is also obtained by the action of sodium phenoxide on *α*-dichloropentane. *α*-Iodo-*ε*-phenoxypentane, prepared by boiling the chloro-derivative with alcoholic sodium iodide, boils at

172—179° under 12 mm. pressure. *α*-Bromo-*ε*-phenoxyptentane, prepared from *αε*-dibromopentane and sodium phenoxide, boils at 162—163° under 12 mm. pressure. *α*-Chloro-*ε*-phenoxyptentane is only slowly attacked by potassium cyanide, but *α*-bromo- and *α*-iodo-phenoxyptentanes are readily converted into *α*-cyano-*ε*-phenoxyptentane, which crystallises from a mixture of ether and light petroleum in long prisms and melts at 36°. *ε*-Phenoxyhexoic acid, $\text{OPh} \cdot [\text{CH}_2]_5 \cdot \text{CO}_2\text{H}$, obtained by hydrolysing the nitrile, crystallises from light petroleum as a white powder and melts at 71°; the *silver* salt was analysed. The *amide*, $\text{OPh} \cdot [\text{CH}_2]_5 \cdot \text{CO} \cdot \text{NH}_2$, formed together with the acid in the hydrolysis of the nitrile, crystallises from dilute alcohol in white leaflets and melts at 99°. W. A. D.

Indirect Fermentative Oxidations. Course of the Reaction in the Oxidation of Quinol. L. MARCHADIER (*J. Pharm. Chim.*, 1905, [vi], 21, 299—302. Compare Bourquelot and Marchadier, *Abstr.*, 1904, ii, 552).—The oxidation of a solution of quinol, with or without the addition of hydrogen peroxide, is greatly accelerated by the addition of a 20 per cent. extract of bran containing toluene and glycerol. Quinone and quinhydrone are formed, and finally the brown products resulting from the oxidation of quinone are obtained. The relative proportions of quinone and quinol in the mixture obtained are dependent on the amount of ferment used. G. D. L.

Action of Bromine and Chlorine on Phenols; Substitution-products, *ψ*-Bromides and *ψ*-Chlorides. Tetrachloro-*p*-dihydroxytolane. THEODOR ZINCKE and H. WAGNER (*Annalen*, 1905, 338, 236—258. Compare *Abstr.*, 1902, i, 282).—Tetrachlorodihydroxytolane, $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CCl} \cdot \text{CH} \\ \text{CCl} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CCl} \\ \text{CH} \cdot \text{CCl} \end{smallmatrix} \text{C} \cdot \text{OH}$, is prepared from tetrachlorodihydroxystilbene, which is acetylated by acetic anhydride in the presence of sulphuric acid, and then converted into the dibromide by bromine in acetic acid solution; the latter yields the tolane derivative when it is heated with a solution of sodium ethoxide in absolute alcohol; the tolane melts at 225—226°. In the last process, tetrachlorodihydroxyhydrobenzoin diethyl ether (m. p. 186°) is formed, and can be isolated by acidifying the alkaline mother liquor.

Tetrachloro-p-dihydroxydeoxybenzoin,

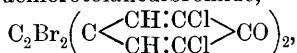


prepared by warming tetrachloro-*p*-dihydroxytolane with concentrated sulphuric acid, crystallises in needles melting at 249°; its *diacetyl* derivative crystallises in prisms melting at 158—159°.

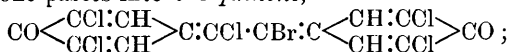
In its action on tetrachlorodihydroxytolane, bromine differs from chlorine in that only two, and not four, atoms are taken up, the *dibromide*, $\text{C}_2\text{Br}_2 \left(\text{C} \begin{smallmatrix} \text{CH} \cdot \text{CCl} \\ \text{CH} \cdot \text{CCl} \end{smallmatrix} \text{C} \cdot \text{OH} \right)_2$, being formed; it crystallises in needles melting and decomposing at 268°, and dissolves in sodium hydroxide with a bluish-violet coloration, acids precipitating a red compound. Prolonged treatment with alkali hydroxide re-

generates the tolane. The *diacetyl* derivative crystallises in needles melting at 212°.

The *quinone* of tetrachlorotolanedibromide,

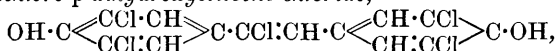


prepared by oxidising the dibromide in the presence of acetic acid by nitric or chromic acids or manganese dioxide, crystallises in yellow plates, becoming red at 235—240°, but not molten at 280°; by boiling with acetic acid and sodium acetate, it can be converted into the tetrachloro-*p*-dihydroxybenzil, and when heated with an acetic acid solution of hydrogen bromide into tetrachloro-*p*-dihydroxytolane dibromide. Treatment with an acetic acid solution of hydrogen chloride converts the quinone into a *ψ-chloride*, $\text{C}_2\text{Cl}_2\text{Br}_2\left(\text{CH}\begin{array}{c} \text{CH}\cdot\text{CCl} \\ \text{CH}\cdot\text{CCl} \end{array}\text{CO}\right)_2$, which crystallises in needles becoming yellow at 120—130°, and melts and decomposes at 222—223°; on heating, it loses 2HBr, yielding a hexachloro-compound (m. p. 248°), and on treatment with a solution of hydrogen chloride in acetic acid it loses HCl and HBr, a stilbene chlorobromide being formed, which on warming with acetic acid or acetone passes into the *quinone*,



the latter crystallises in reddish-yellow prisms or needles melting and decomposing at 218—219°. It is reduced by stannous chloride in acetic acid solution to *tetrachloro-p-dihydroxytolane chlorobromide*, which crystallises in needles melting at 258—259°; its *diacetyl* derivative melts at 191°.

Hydrogen chloride in acetic acid solution forms an additive product, *tetrachloro-p-dihydroxystilbene chloride*,



with the tolane derivative, the additive product with 2 mols. of hydrogen chloride, tetrachloro-*p*-dihydroxydibenzyl-*ψ*-chloride, being formed at the same time; the stilbene derivative crystallises in needles melting at 197°, and is converted into a quinone by nitric acid and into the original tetrachloro-*p*-dihydroxytolane by boiling with alkalis. The *diacetyl* derivative forms prismatic needles melting at 162°. The corresponding *stilbene bromide* is formed together with the analogous dibromodibenzyl derivative when hydrogen bromide is substituted for hydrogen chloride, and crystallises in needles melting at 185°; its *diacetyl* derivative crystallises in needles sintering at 132° and melting at 136—137°.

Tetrachloro-*p*-dihydroxytolane is readily oxidised by all agents to a red compound, which is best prepared by using potassium ferri-cyanide in alkaline solution; the compound, which is taken to be the *quinhydrone*, $\text{O}\begin{array}{c} \text{C}_6\text{H}_2\text{Cl}_2(\text{OH})\cdot\text{C}\cdot\text{C}\cdot\text{C}_6\text{H}_2\text{Cl}_2(\text{OH}) \\ \text{C}_6\text{H}_2\text{Cl}_2\text{-----C}\cdot\text{C}\text{-----C}_6\text{H}_2\text{Cl}_2 \end{array}\text{O}$, corresponding with tetrachlorotolanequinone, crystallises in red needles or plates melting at 202—207°, and dissolves in alkali hydroxides with a blue coloration; from this solution, the compound is precipitated unchanged, but on keeping is converted into the original tetrachloro-dihydroxytolane.

K. J. P. O.

[*p*-Methoxyphenylethylcarbinol.] AUGUST KLAGES (*Ber.*, 1905, 38, 912—914. Compare Abstr., 1902, i, 609).—A reply to Hell and Hofmann (this vol., i, 58). The author has repeated the preparation of *p*-methoxyphenylethylcarbinol and confirms his previous statements (*loc. cit.*) in all details.

If anisaldehyde and magnesium ethyl bromide are allowed to react in the cold and the mixture treated with ice and dilute sulphuric acid, the main product obtained is the *ether* of methoxyphenylethylcarbinol, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHEt})_2\text{O}$, which is a colourless, viscid oil; it boils at 215—216° under 17 mm. pressure, and has a sp. gr. 1.057 at 17°/4°, and n_D 1.5394 at 17°. G. Y.

p-Methylaminobenzoic Acid. MAX JAFFÉ (*Ber.*, 1905, 38, 1208—1212. Compare Abstr., 1905, ii, 186).—The identity of the supposed *p*-methylaminobenzoic acid, isolated from the urine of animals fed on *p*-dimethylaminobenzaldehyde, has been established by its preparation synthetically by the action of methyl iodide, potassium hydroxide and methyl alcohol on *p*-aminobenzoic acid. So obtained, it crystallises in colourless or faintly yellow needles, melting at 155—157°, and gives no precipitate on the addition of lead acetate to the aqueous solution; it forms an emerald-green, crystalline *copper* salt, a bluish-green, amorphous *basic copper* salt and a colourless *silver* salt crystallising in microscopic needles. The *nitroso*-derivative separates from alcohol in glistening, yellow needles melting at 195—196°. An acid melting at 228—229° has been described by Houben as *p*-methylaminobenzoic acid (Abstr., 1904, i, 1014).

E. F. A.

Compounds of Formaldehyde with the Amides of Mono-basic Acids. ALFRED EINHORN (D.R.-P. 157355).—Formaldehyde condenses with amides in the presence of acid condensing agents to form diacyl derivatives of methylenediamine, such as methylenedibenzamide. When alkaline condensing agents are employed, however, compounds having the general formula $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$ are obtained.

Hydroxymethylbenzamide, $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$, crystallises from acidified water in hexagonal tablets and melts at about 104—106°; it dissolves in alcohol, ethyl acetate, benzene, or chloroform, sparingly in water. *Hydroxymethyl-p-toluamide* crystallises from alcohol in needles and melts at 102—104°. *Hydroxymethylsalicylamide* crystallises from water in prismatic needles and melts at 128°; *hydroxymethyl-p-hydroxybenzamide* forms white needles, melts at 155°, and reduces ammoniacal silver solution. *Hydroxymethylisovaleramide* forms felted needles and melts at 69—71°; *hydroxymethylguaiacolacetamide*, from guaiacoxylacetamide, forms felted needles and melts at 80°. Asparagine yields a highly condensed product. C. H. D.

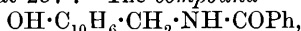
Acyl Derivatives of Benzylamine. ALFRED EINHORN (D.R.-P. 156398).—The hydroxymethyl derivatives of amides react with a large number of aromatic compounds in presence of condensing agents to form acyl derivatives of benzylamine. In a few cases, when acids are employed, methylenediamides are also produced.

Hydroxymethylbenzamide, $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot OH$, from benzamide and formaldehyde, crystallises from benzene or chloroform, melts at $104-106^\circ$, and dissolves sparingly in water, readily in alcohol. It condenses with *p*-nitrophenol to form *benzoyl-m-nitro-o-hydroxybenzylamine*, melting at $217-218^\circ$. *Hydroxymethylchloroacetamide* crystallises from acetone in leaflets and melts at $97-99^\circ$. It condenses with *p*-nitrophenol in presence of cold concentrated sulphuric acid to form *chloroacetyl-m-nitro-o-hydroxybenzylamine*,



which crystallises from alcohol in needles and melts at 182° .

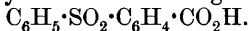
Dihydroxymethylsuccinamide forms crystalline aggregates and melts and decomposes at 158° . It condenses with *p*-nitrophenol to form the compound $C_2H_4[CO \cdot NH \cdot CH_2 \cdot C_6H_3(NO_2) \cdot OH]_2$, crystallising in small, white needles which become yellow on separating from nitrobenzene and melting at 257° . The compound



from hydroxymethylbenzamide, β -naphthol, and hydrochloric acid, crystallises from alcohol in prisms and melts at $185-186^\circ$. *Benzoylbenzylaminocarboxylic acid*, $COPh \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$, from hydroxymethylbenzamide and benzoic acid, melts at 190° . The compound from hydroxymethylchloroacetamide and benzoic acid forms needles and melts at 176° ; the corresponding compound from salicylic acid melts at 196° . The compound from hydroxymethylchloroacetamide and acetanilide forms prisms and melts at 206° . Benzene condenses with dihydroxymethylsuccinamide in presence of sulphuric acid to form the compound $C_6H_4 \begin{matrix} < CH_2 \cdot NH \cdot CO \cdot CH_2 \\ < CH_2 \cdot NH \cdot CO \cdot CH_2 \end{matrix}$, an amorphous, yellow substance,

which becomes brown at 200° and melts and decomposes at about 225° . The same amide condenses with β -naphthol to form a compound melting at $222-224^\circ$, and with *m*-xylene-4-sulphonic acid to form a white, crystalline compound which remains unmelted at 260° . C. H. D.

Diphenylsulphone-*o*-carboxylic Acid and Related Compounds. WILLIAM S. WEEDON and HOWARD W. DOUGHTY (*Amer. Chem. J.*, 1905, **33**, 386—430. Compare Graebe and Schultess, *Abstr.*, 1891, 1058).—By the action of dilute nitric acid on phenylthiosalicylic acid, Graebe and Schultess obtained a substance which they termed "sulphobenzide-*o*-carboxylic acid" and assigned the formula



On repeating this work, it has been found that the product of the reaction consists almost entirely of *diphenylsulphoxide-o-carboxylic acid*, $C_6H_5 \cdot SO \cdot C_6H_4 \cdot CO_2H$, which crystallises from methyl alcohol in long, colourless prisms, melts at 163° , and is readily soluble in alcohol or chloroform and sparingly so in ether or hot water; it crystallises from water with $1H_2O$. The *barium*, *strontium*, and *calcium* salts are described.

When phenylthiosalicylic acid is treated with fuming nitric acid, a product is obtained which has the melting point of the substance described by Graebe and Schultess. This product, however, is not a single substance, but a mixture of diphenylsulphoxide-*o*-carboxylic acid and a nitro-derivative of this acid.

Nitrodiphenylsulphoxide-o-carboxylic acid, $NO_2 \cdot C_6H_4 \cdot SO \cdot C_6H_4 \cdot CO_2H$,

separates from hot benzene in small, colourless crystals and melts at 222° (corr.); its *barium* salt is described. The yield of this acid is increased by boiling the phenylthiosalicylic acid with fuming nitric acid. When phenylthiosalicylic acid is heated with a mixture of fuming nitric acid and sulphuric acid, a product is obtained which is probably a mixture of di- and tri-nitrophenylsulphoxide-*o*-carboxylic acids together with some of the mononitro-compound.

By the action of potassium permanganate on phenylthiosalicylic acid, *diphenylsulphone-o-carboxylic acid*, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is produced, which crystallises from benzene in white needles, melts at 146° , and is very soluble in alcohol, ether, glacial acetic acid, or acetone; when crystallised from water, it is obtained as efflorescent prisms with $1.5\text{H}_2\text{O}$ and melts at 51.5° . This compound is not identical with the *o*-phenylsulphonebenzoic acid described by Canter (Abstr., 1901, i, 208). The *calcium*, *barium*, and *strontium* salts of diphenylsulphone-*o*-carboxylic acid are described. The *chloride* crystallises in colourless prisms or needles and melts at 80° (corr.); the *amide* forms white, slender needles and melts at $175\text{--}175.5^{\circ}$ (corr.); the *anhydride* separates from hot alcohol in small, colourless crystals and melts at 148° (corr.). The *ethyl* ester crystallises in feathery needles and melts at $78\text{--}79^{\circ}$ (corr.); the *methyl* ester separates from methyl alcohol in rectangular plates and melts at 63° . When diphenylsulphone-*o*-carboxylic acid is heated with concentrated sulphuric acid, benzophenonesulphone is produced, which is identical with the compound obtained by Graebe and Schultess by the oxidation of thioxanthone with chromic acid.

When phenylthiosalicylic acid is heated with lime, phenyl sulphide is produced. If diphenylsulphone-*o*-carboxylic acid is treated in a similar manner, diphenylsulphone is obtained.

When phenyl *o*-tolyl sulphide is oxidised with potassium permanganate, diphenylsulphone-*o*-carboxylic acid is produced.

By the oxidation of phenyl-*o*-tolylsulphone with potassium permanganate, Canter (*loc. cit.*) obtained a compound which he supposed to be diphenylsulphone-*o*-carboxylic acid. On repeating his experiments, it has been found that the product is not diphenylsulphone-*o*-carboxylic acid, but is the isomeric *p*-phenylsulphonebenzoic acid first described by Newell (Abstr., 1898, i, 430). The formation of this compound under the conditions of Canter's investigation is due to the presence of *p*-toluenesulphonic chloride in the *o*-toluenesulphonic chloride used in the preparation of the phenyl-*o*-tolylsulphone. When, however, pure phenyl-*o*-tolylsulphone is treated with potassium permanganate, diphenylsulphone-*o*-carboxylic acid is the sole product of the reaction.

p-Phenylsulphonebenzoic acid, $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by the action of thiophenol on the solution obtained by the diazotisation of *p*-aminobenzoic acid, crystallises from alcohol in colourless, hexagonal plates and melts at 177° (corr.); its *barium* salt is described. On oxidation with potassium permanganate, it is converted into *p*-phenylsulphonebenzoic acid, which melts at 277° (corr.); the *barium* salt was prepared and analysed. *p*-Phenylsulphonebenzoyl chloride melts at $146\text{--}147^{\circ}$ (corr.), and the amide melts at $248.3\text{--}248.8^{\circ}$ (corr.).

E. G.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. V. Reactions with α -Cyanocinnamic Acid. ELMER P. KOHLER and MARIE REIMER (*Amer. Chem. J.*, 1905, 33, 333—356. Compare Abstr., 1904, i, 595; this vol., i, 207, 208).—Ethyl α -cyanocinnamate can be prepared in theoretical yield by a slight modification of the method described by Carrick (Abstr., 1892, 1086). When a solution of this ester in ether or benzene is added to a boiling solution of magnesium phenyl bromide, a magnesium compound is obtained which, on decomposition with water, yields *ethyl α -cyano- $\beta\beta$ -diphenylpropionate*, $\text{CHPh}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, which crystallises from alcohol in large, colourless pyramids, melts at 78° , and is readily soluble in chloroform, acetone, or hot alcohol, and fairly so in ether or cold alcohol. *α -Cyano- $\beta\beta$ -diphenylpropionic acid* crystallises in small, colourless needles, melts at 162° , and is very soluble in alcohol or ether and slightly so in light petroleum or hot water. When the acid is heated at 190° , it undergoes decomposition with evolution of carbon dioxide and formation of *$\beta\beta$ -diphenylpropionitrile*, $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{CN}$, which crystallises in small, lustrous prisms, melts at 100° , and is readily soluble in most organic solvents. *$\beta\beta$ -Diphenylpropionamide* crystallises in needles, melts at 127° , and is readily soluble in alcohol or ether and very slightly so in water. *$\beta\beta$ -Diphenylmethylmalonamic acid*, $\text{CHPh}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}_2$, obtained by boiling ethyl cyanodiphenylpropionate with aqueous potassium hydroxide and acidifying the product, crystallises in long, slender needles and is readily soluble in alcohol and moderately so in ether; its melting point depends largely on the rate of heating, since the substance easily suffers decomposition with evolution of carbon dioxide and formation of diphenylpropionamide; when heated for a short time at 150° , it is decomposed completely.

Ethyl α -bromo- α -cyano- $\beta\beta$ -diphenylpropionate,
 $\text{CHPh}_2\cdot\text{CBr}(\text{CN})\cdot\text{CO}_2\text{Et}$,

obtained by the action of bromine on the magnesium compound formed by adding magnesium phenyl bromide to ethyl α -cyanocinnamate, crystallises in large, colourless prisms, melts at 97° , and is readily soluble in chloroform or acetone and moderately so in alcohol or ether. On hydrolysis with potassium hydroxide, the ester is converted into *α -cyano- $\beta\beta$ -diphenylcinnamic acid*, $\text{CPh}_2\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{H}$, which crystallises in needles, melts at 178° , decomposes above 190° , and is readily soluble in alcohol, ether, or chloroform, and sparingly so in light petroleum or hot water; when boiled with alcoholic potassium hydroxide, a small quantity of *$\beta\beta$ -diphenylcinnamic acid* is produced, together with a larger proportion of *$\beta\beta$ -diphenylcinnamonitrile*, $\text{CPh}_2\cdot\text{CH}\cdot\text{CN}$, which forms long, pale yellow needles and melts at 49° .

When the magnesium compound is treated with a solution of acetyl chloride in benzene, a compound, $(\text{C}_7\text{H}_8\text{O}_3\text{N})_2\text{Mg}\cdot 2\text{H}_2\text{O}$, is obtained which crystallises in small, lustrous prisms, and, when treated with dilute hydrochloric acid, is converted into ethyl cyanoacetate. The filtrate from this substance yields a crystalline compound,

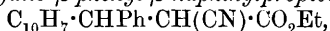
$\text{CHPh}_2\cdot\text{C}(\text{CN})\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot\text{CHPh}_2$,

which melts at 156° , is not decomposed at 300° , and is readily soluble in chloroform or hot glacial acetic acid; when heated with concentrated

hydrochloric acid for 8 hours at 225°, it is decomposed with formation of benzhydrol ether, diphenylpropionic acid, alcohol, carbon dioxide, and ammonia; the same substance can be prepared by treating the magnesium compound with diphenylbromomethane.

By the action of benzoyl chloride on the magnesium compound, magnesium ethyl cyanobenzoylacetate is produced together with the compound just described, which melts at 156°.

By the action of magnesium α -naphthyl bromide on ethyl α -cyanocinnamate, *ethyl α -cyano- β -phenyl- β -naphthylpropionate*,



is produced, which crystallises in minute plates, melts at 132°, and is readily soluble in chloroform or ethyl acetate. *β -Phenyl- β -naphthylmethylmalonamic acid*, $\text{C}_{10}\text{H}_7\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}_2$, obtained by boiling the ester with alcoholic potassium hydroxide, decomposes at 170–180°, and on oxidation is converted into α -naphthophenone.

When ethyl α -cyanocinnamate is treated with magnesium methyl iodide, ethyl α -cyano- β -phenylbutyrate is produced. *α -Cyano- β -phenylbutyric acid*, $\text{CHPhMe}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{H}$, crystallises in colourless prisms, melts at 130°, decomposes at 180°, and is readily soluble in alcohol, ether, or chloroform, and sparingly so in light petroleum. *β -Phenylethylmalonamic acid*, $\text{CHPhMe}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}_2$, crystallises in needles and melts and decomposes at 172°; when heated at 180°, it is converted into *β -phenylbutyramide*, which forms white, slender needles, melts at 105°, and is very soluble in alcohol or ether. *β -Phenylbutyric acid*, $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was obtained as an oil by hydrolysing the amide; its *sodium* salt is described.

By the action of magnesium benzyl chloride on ethyl α -cyanocinnamate, an oily ester was obtained which, on boiling with alcoholic potassium hydroxide, was converted into *$\beta\gamma$ -diphenylethylmalonamic acid*, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{NH}_2$, which crystallises in slender needles, melts and decomposes at about 182°, and is oxidised by potassium permanganate with formation of deoxybenzoin. *$\beta\gamma$ -Diphenylbutyramide*, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, crystallises in thick, long needles and melts at 62°.

When ethyl α -cyanocinnamate is treated with magnesium isopropyl bromide, an oily product is obtained which, on hydrolysis with potassium hydroxide, is converted into the compound $\text{C}_{13}\text{H}_{19}\text{O}_3\text{N}$, which crystallises in slender needles and melts and decomposes at 176°.

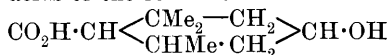
By the action of magnesium phenylacetylene bromide on ethyl α -cyanocinnamate, the *ester*, $\text{CPh}\cdot\text{C}\cdot\text{CHPh}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, is obtained, which crystallises in colourless needles, melts at 80°, and is readily soluble in hot alcohol and moderately so in cold alcohol or ether. E. G.

Constitution of the so-called Hagemann's Ester. PAUL RABE and FRITZ RAHM (*Ber.*, 1905, 38, 969–973).—Hagemann's ester, obtained by the action of methylene iodide on ethyl sodioacetate (Abstr., 1893, i, 393), is *ethyl 2-methylcyclo- Δ^2 -hexene-4-one-1-carboxylate*, $\text{CO}_2\text{Et}\cdot\text{CH}\left\langle\begin{array}{c} \text{CMe}\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH}_2 \end{array}\right\rangle\text{CO}$, and not the β -ketonic ester, $\text{CO}_2\text{Et}\cdot\text{CH}\left\langle\begin{array}{c} \text{CO}\cdot\text{CH} \\ \text{CH}_2\cdot\text{CH}_2 \end{array}\right\rangle\text{CMe}$, as supposed by Callenbach (Abstr.,

1897, i, 271). That this is so is shown by the fact that it is obtained from ethyl 6-methylcyclohexane-6-ol-4-one-1:3-dicarboxylate, $\text{CO}_2\text{Et}\cdot\text{CH}<\begin{smallmatrix} \text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et}) \\ \text{CMe}(\text{OH})-\text{CH}_2 \end{smallmatrix}>\text{CO}$ (Abstr., 1904, i, 747), by the elimination of water and one carbethoxyl group under the influence of sodium ethoxide, and by its giving ethyl 4-hydroxy-2-methylbenzoate (Claisen, Abstr., 1897, i, 592) under the action of bromine in carbon disulphide solution. Both the "acid" and "neutral" esters of Hagemann give the same result in the latter case and both give also the same *semicarbazone*, $\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}_3$, which crystallises from alcohol in slender, white needles melting at 169° . The relationship between these substances will be considered in a future paper.

W. A. D.

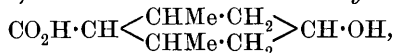
Constitution of the cycloHexenonecarboxylic Esters. GEORG MERLING [with ROBERT WELDE and ALADAR SKITA] (*Ber.*, 1905, **38**, 979—985).—On reducing ethyl isophoroncarboxylate [ethyl 2:6:6-trimethylcyclo- Δ^2 -hexene-4-one-1-carboxylate] (Abstr., 1903, i, 317) with sodium and alcohol, a mixture of three pairs of *cis-trans*-isomeric hydroxy-acids of the formula



is obtained; on heating these acids with dilute sulphuric acids, three stable *lactones*, melting respectively at 44° , 58° , and 39° , are formed, showing that in the parent ketonic acid the carboxyl and carbonyl groups occupy a para-position relatively to each other. The lactones are oxidised by Beckmann's solution to three stereoisomeric *keto-dihydrocyclogeranic acids* or *dihydroisophoroncarboxylic acids*, $\text{CO}_2\text{H}\cdot\text{CH}<\begin{smallmatrix} \text{CMe}_2-\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CO}$, melting at $123\text{--}124^\circ$, $127\text{--}128^\circ$, and $118\text{--}119^\circ$ respectively, which boil at $178\text{--}179^\circ$ under 11 mm. pressure and lose carbon dioxide when heated above 200° ; this fact proves them to be para- and not ortho-ketonic acids.

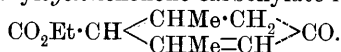
Ethyl isophoroncarboxylate (2:6:6-trimethylcyclo- Δ^2 -hexene-4-one-1-carboxylate) is stable towards boiling dilute sulphuric acid, but by boiling aqueous barium hydroxide is resolved into carbon dioxide, alcohol, and isophorone. The ester exists in two modifications, one soluble and the other insoluble in aqueous alkalis; the former is probably the enolic modification, $\text{CO}_2\text{Et}\cdot\text{CH}<\begin{smallmatrix} \text{CMe}_2\cdot\text{CH} \\ \text{CMe}=\text{CH} \end{smallmatrix}>\text{C}\cdot\text{OH}$.

Knoevenagel's dimethylcyclohexenonecarboxylic esters (*Annalen*, 1894, **281**, 109) are also probably δ -ketonic esters; on reduction with sodium and alcohol, a mixture of stereoisomeric *hydroxy-acids*,



is obtained, which has not yet been resolved into its constituents; on oxidation, the mixed acids give a mixture of ketonic acids having the formula $\text{CO}_2\text{H}\cdot\text{CH}<\begin{smallmatrix} \text{CHMe}\cdot\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2 \end{smallmatrix}>\text{CO}$; this mixture is not decomposed when distilled at $169\text{--}174^\circ$ under 10 mm. pressure, and the acids therefore belong to the δ -ketonic and not to the β -ketonic series. The

original ethyl dimethylcyclohexenone-carboxylate is therefore



Similar considerations would apply to the so-called Hagemann's ester, which is therefore a δ -ketonic ester (compare Rabe and Rahm, this vol., i, 348).

In conclusion, the nature of the condensation of ethyl sodioacetoacetate with ethyl isopropylideneacetoacetate is discussed.

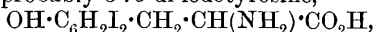
W. A. D.

Oxidation of Indigo by Potassium Permanganate. N. CHOLIN (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1521—1524).—It has been observed that, if synthetical crystalline indigotin is converted into indigotindisulphonic acid and then oxidised to sulphoisatin by means of potassium permanganate solution, the amount of the latter used up is less by about 13 per cent. than that calculated from the equation: $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2 + \text{O}_2 = \text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_2$. The author finds that this is not due to a portion of the indigotin undergoing oxidation during the sulphonation, thus: $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2 + 2\text{H}_2\text{SO}_4 = \text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_2 + 2\text{SO}_2 + 2\text{H}_2\text{O}$, as has been suggested.

On treating a cooled solution of indigotin in carbon tetrachloride with 4 mols. of chlorine or bromine, the theoretical quantity of halogen is absorbed, but further investigation shows that the product consists (when bromine is employed) of a mixture of unaltered indigotin with the mono-, $\text{C}_{16}\text{H}_9\text{O}_2\text{N}_2\text{Br}$, and di-bromo-derivatives, $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\text{Br}_2$.

T. H. P.

Synthesis of Iodogorgonic Acid. HENRY L. WHEELER and GEORGE S. JAMIESON (*Amer. Chem. J.*, 1905, **33**, 365—372. Compare Henze, Abstr., 1903, i, 668).—It is shown that iodogorgonic acid is a di-iodotyrosine, probably 3:5-di-iodotyrosine,



and that it can be prepared by adding rather less than the calculated quantity of iodine to a solution of *l*-tyrosine in presence of alkali hydroxide. The substance is soluble in water at 25° to the extent of 0.2 per cent., but is much more soluble in hot water. By the action of hydriodic acid, or of zinc and hydrochloric acid, it is converted into tyrosine. Di-iodotyrosine *hydrochloride* and *sulphate*, and the *silver*, *copper*, and *lead* salts are described; the *acetyl* derivative forms a yellow powder which is sparingly soluble in alcohol and decomposes at about 225°.

E. G.

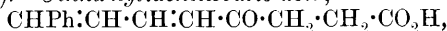
4-*p*-Hydroxyphenylsalicylic Acid. J. FAURE (*Bull. Soc. chim.*, 1905, [iii], **33**, 348—351).—4-*p*-Hydroxyphenylsalicylic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$, prepared by Tiemann and Reimer's method (Abstr., 1877, i, 77), using *p*-diphenol as a starting point, separates from boiling dilute alcohol in small, colourless crystals, melts at 225°, dissolves in water to the extent of 0.22 and 4.4 per cent. at 19° and 98° respectively, is readily soluble in chloroform, ether, or warm alcohol, and gives a yellow coloration with calcium hypochlorite and blue with ferric chloride. When heated with lime, it loses carbon dioxide and

forms diphenol. The *sodium, potassium, ammonium, calcium, magnesium, zinc, nickel, cobalt, and lead* salts were prepared.

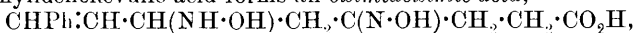
T. A. H.

Cinnamylidenelævulinic Acid and its Reduction Products.

HANS RUPE and FELIX SPEISER (*Ber.*, 1905, **38**, 1113—1125. Compare this vol., i, 220).—*Cinnamylidenelævulic acid*,

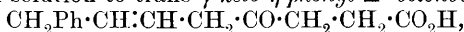


is formed when cinnamaldehyde and lævulic acid are heated with pyridine in a reflux apparatus at 144—155° for 24 hours. It crystallises in large, transparent, highly refractive, yellow crystals, melts at 161°, and is easily soluble in most organic solvents. The *silver, copper, barium, calcium*, $(\text{C}_{14}\text{H}_{13}\text{O}_3)_2\text{Ca}\cdot 4\text{H}_2\text{O}$, and *magnesium* salts are described. The *ethyl* ester, $\text{C}_{16}\text{H}_{18}\text{O}_3$, crystallises in long, green needles and melts at 82°; the *methyl* ester crystallises in yellow leaflets and melts at 88°. With hydroxylamine in alkaline solution, cinnamylidenelævulic acid forms an *oximidoziminic acid*,

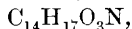


which crystallises in delicate yellow leaflets, decomposes at 130°, and dissolves in aqueous sodium hydroxide on warming. The *tetrabromide*, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Br}_4$, formed by the action of bromine on the acid in chloroform solution, crystallises from alcohol and melts at 203°; the *ethyl* ester, $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Br}_4$, crystallises in glistening, white needles and melts at 152°.

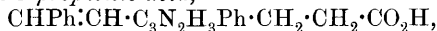
Cinnamylidenelævulic acid is reduced by sodium amalgam in dilute sulphuric acid solution to *trans-γ-keto-η-phenyl-Δ^ε-octenoic acid*,



which crystallises in large, colourless prisms, melts at 96°, is easily soluble in most organic solvents, decolorises alkaline potassium permanganate solution, and when boiled with aqueous alkali carbonates yields a volatile oil. The *salts* are mostly easily soluble in water, and on concentration of their solutions are decomposed with evolution of carbon dioxide; the *silver* salt, $\text{C}_{14}\text{H}_{15}\text{O}_3\text{Ag}$, is very sensitive to light. The *ethyl* ester, $\text{C}_{14}\text{H}_{15}\text{O}_3\text{Et}$, is a yellow oil which boils at 203° under 14 mm. pressure, and under the atmospheric pressure distils with slight decomposition; the *methyl* ester is an oil which boils at 204—205° under 16 mm. pressure. With hydrogen bromide in glacial acetic acid solution, the acid forms *ε-bromo-γ-keto-η-phenyloctoic acid*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in long, colourless prisms, melts at 79°, and rapidly decomposes in a vacuum, less rapidly on exposure to the air. With hydroxylamine in aqueous solution, the unsaturated keto-acid forms an *oxime*,



which crystallises in slender needles and melts at 122°. 1-*Phenyl-5-styrylpyrazoline-3-propionic acid*,



is formed by the action of phenylhydrazine on the hydrobromide of the keto-acid; it crystallises in slender, white needles, melts at 138°, is easily soluble in alcohol, ether, benzene, or cold aqueous sodium carbonate solution, and with ferric chloride or potassium dichromate in acid solution gives transitory violet to purple and red colorations.

When treated with bromine in a neutral solvent, the *trans*-acid forms a dibromide, which, when warmed with concentrated aqueous potassium carbonate solution, is converted into *cis*- γ -keto- η -phenyl- Δ^{α} -octenoic acid. This crystallises in thick, colourless plates or long, transparent, triclinic (?) prisms, melts and changes into the *trans*-acid at 71°, is easily soluble in the usual organic solvents, and decolorises potassium permanganate. The *barium* and *calcium* salts are easily soluble in water; the *alkali* salts decompose on concentration of their aqueous solutions; the white, unstable *silver* salt crystallises in white needles. The *oxime* of the *cis*-acid crystallises in nacreous leaflets and melts at 120–121°. With hydrogen bromide in glacial acetic acid, the *cis*-acid yields the same hydrobromide as is obtained from the *trans*-acid. α -Phenyl- Δ^{β} -hepten- ϵ -one, $\text{CH}_2\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, is formed along with the *cis*-acid by the action of aqueous potassium carbonate on the dibromide of the *trans*-acid. It is an oil which distils with partial decomposition at 230–236° under 14 mm. pressure, is insoluble in aqueous potassium carbonate, and forms a *semicarbazone*, $\text{C}_{14}\text{H}_{19}\text{ON}_3$, crystallising in glistening, white, silky needles. G. Y.

2-Methoxystilbene. CASIMIR FUNK and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 939–940).—2-Methoxystilbene- β -carboxylic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CPh}\cdot\text{CO}_2\text{H}$, is readily obtained by the condensation of phenylacetic acid with salicylaldehyde methyl ether according to Ogialoro's method; it crystallises from alcohol in colourless needles, melts at 186–187°, and when distilled yields α -phenylcoumarin.

2-Methoxystilbene may be obtained by leaving the acid in contact with hydriodic acid of sp. gr. 1.96 for several days. It crystallises from dilute alcohol in plates melting at 70°.

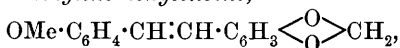
3-Methoxystilbene- β -carboxylic acid melts at 189° and does not yield 3-methoxystilbene when treated in a similar manner. J. J. S.

Stilbene Derivatives. STANISLAUS VON KOSTANECKI and J. SULSER (*Ber.*, 1905, **38**, 941–942. Compare preceding abstract).—Three

isomeric acids, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CO}_2\text{H})\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix}\text{CH}_2$, have been obtained by condensing sodium homopiperonalate with the three isomeric methoxybenzaldehydes in the presence of acetic anhydride at 150–170°.

2-Methoxy-3':4'-methylenedioxy stilbene- β -carboxylic acid crystallises in small needles and melts at 225–226°; the isomeric 3-methoxy-compound forms stout needles and melts at 204–205°, and the 4-methoxy-derivative melts at 199–200°. The acids lose carbon dioxide when kept for several days in closed vessels with concentrated hydriodic acid.

2-Methoxy-3':4'-methylenedioxy stilbene,



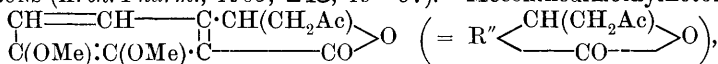
crystallises in prisms and melts at 99–100°; the isomeric 4-methoxy-derivative melts at 153–154°, but the 3-methoxy-compound has not been isolated.

2:4-Dimethoxystilbene- β -carboxylic acid, $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}:\text{CPh}\cdot\text{CO}_2\text{H}$,

melts at 196—198°, and 2:4-dimethoxy-3':4'-methylenedioxy stilbene- β -carboxylic acid, $C_6H_3(OMe)_2 \cdot CH \cdot C(CO_2H) \cdot C_6H_3 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} CH_2$, melts at 203°.

J. J. S.

Products of the Condensation of Opianic Acid. DANIEL BRUNS (*Arch. Pharm.*, 1905, **243**, 49—57).—Meconinedimethylketone,



is obtained when opianic acid is allowed to react with acetone, CH_3Ac , in the presence of an alkali, and the product is acidified (Goldschmiedt, *Abstr.*, 1892, 179; Hemmelmayer, *Abstr.*, 1894, i, 151; compare also Book, *Abstr.*, 1902, i, 464); in neutral and acid solutions, no condensation occurs. The substance does really behave like a lactone, for it reacts slowly with an alkali instead of neutralising at once as much as would correspond with the isomeric acid $CHAc \cdot CH \cdot R'' \cdot CO_2H$. The lactone of which it is derivative, $R'' \begin{array}{c} CH(OH) \\ \diagup \quad \diagdown \\ CO \end{array} O$, is a tautomeric form of the aldehyde acid, $CHO \cdot R'' \cdot CO_2H$, and stands to it in the same relation as the carbinol form to the aldehydic form of a ψ -ammonium base (this vol., i, 368). The true methyl ester of opianic acid, $CHO \cdot R'' \cdot CO_2Me$ (Wegscheider, *Abstr.*, 1893, i, 167), does not condense with acetone.

A compound of opianic acid with chloroform could not be obtained.

C. F. B.

Condensation of Aminobenzoic Acids with Ethyl Malonate.

WALTER VON POLLACK (*Monatsh.*, 1905, **26**, 327—334. Compare Schiff, *Abstr.*, 1886, 549).—When heated together without a solvent, at 165—170°, anthranilic acid and ethyl malonate form *o*-malonaminobenzoic acid, $CH_2(CO \cdot NH \cdot C_6H_4 \cdot CO_2H)_2$, which crystallises in slender, white needles and melts and decomposes at 242°. *p*-Malonaminobenzoic acid, obtained in the same manner, decomposes at 276°. The *o*- and *p*-acids distil, with partial decomposition, in a vacuum, and are easily soluble in concentrated sulphuric acid, from their solutions in which they are precipitated unchanged on addition of water. *m*-Malonaminobenzoic acid, formed in the same manner as its isomerides, decomposes at 258—259°.

These acids form crystalline salts, of which the sodium (+3H₂O) and silver salts of the *o*- and the silver salts of the *p*-acid were analysed. The *o*- and *p*-acids form crystalline *diphenylhydrazones*, $C_{29}H_{26}O_4N_6$, which decompose above 360°. On addition of hydrochloric acid to the cooled aqueous alkaline solution of potassium nitrite and *o*-malonaminobenzoic acid, the *dinitroso*-derivative, $C_{17}H_{12}O_3N_4$, is obtained as a yellow, flocculent precipitate, which decomposes above 350°.

When heated at their melting points, the three malonaminobenzoic acids lose carbon dioxide and form similar, brown, tarry products.

G. Y.

Methylated Tannin. JOSEF HERZIG and RUDOLF TSCHERNE (*Ber.*, 1905, **38**, 989—991).—*Methyl tannin*, prepared by the action of diazomethane on an ethereal solution of tannin, separates from ethyl alcohol as a colourless, amorphous powder and melts at 124—126°. Its probable composition is represented by $C_{24}H_8O_7(OMe)_8$ or $C_{25}H_{10}O_7(OMe)_8$. Gallic acid is produced by the action of hydriodic acid on it. Methyl tannin is dextrorotatory. When heated with potassium hydroxide, it forms a mixture of trimethyl gallic acid and dimethyl gallic acid (3 : 4 : 5-trimethoxybenzoic and 5-hydroxy-3 : 4-dimethoxybenzoic acids).
A. McK.

Characterisation of Aromatic Aldehydes and Ketones. PAVEL IW. PETRENKO-KRITSCHENKO and F. DOLGOPOLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1505—1509. Compare Petrenko-Kritschenko and Eltschaninoff, *Abstr.*, 1903, i, 440 ; Petrenko-Kritschenko and Kestner, *Abstr.*, 1903, ii, 719 ; Kldiaschwili, *Abstr.*, 1903, ii, 719).—The authors have measured the velocities of the reactions of a number of aldehydes and ketones with phenylhydrazine and with potassium hydrogen sulphite, the results showing that aromatic ketones react considerably more slowly than the corresponding aliphatic compounds, whilst with aldehydes the reverse is the case. Investigation of the effect produced on the speed of the reaction by the introduction of methylene groups shows that closed-chain compounds, to which Baeyer's tension theory attributes a ring-angle greater than a right angle (namely, rings with 5, 6, 7, or 8 members), exhibit velocities of reaction less than those of the corresponding open-chain compounds. Where this angle is less than a right angle, the reverse holds.

The authors explain the difference in behaviour between aromatic ketones and aldehydes by supposing that in both cases the symmetry of the benzene nucleus is disturbed, the ring-angle for the ketones approximating to the magnitude of the angle of a 7- or 8-atom ring, whilst in the case of aromatic aldehydes the ring-angle is diminished to approximately the value it possesses in a tetramethylene ring.

T. H. P.

Oxidation of Benzaldehyde in the presence of Acetic Anhydride. WILLEM P. JORISSEN and WILHELM E. RINGER (*Chem. Centr.*, 1905, i, 817—818 ; from *Chem. Weekblad*, **2**, 19—39).—When a mixture of benzaldehyde (1 mol.) and acetic anhydride (2 mols.) with or without admixture of sand is exposed in diffused light and in a closed vessel to an atmosphere of oxygen, benzoyl acetyl peroxide is obtained. In opposition to the observation of Baeyer and Villiger (*Abstr.*, 1900, i, 437), the compound is only slowly resolved on warming with 10 per cent. sodium hydroxide into benzoyl peroxide. When the mixture is exposed to air in a dish with small surface, oxidation is slow and benzoic acid is formed, whilst in larger dishes benzoyl acetyl peroxide is also produced.

Diffused daylight greatly accelerates the oxidation without, however, a period of induction or after-effect. The light from a Welsbach burner is inactive, but the electric arc is extraordinarily active, a

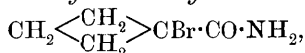
marked after-effect, but no period of induction, being noticed. When passed through a red glass plate, the electric light is inactive, but when passed through a violet plate is again active, showing both a period of induction and after-effect. Magnesium light similarly accelerates the oxidation with a short period of induction and more prolonged after-effect, but when allowed to pass through the space in which the mixed vapours are present, no effect is noticed, owing probably to the small vapour pressure of the aldehyde. Röntgen and radium rays are inactive.

G. D. L.

Preparation of Aldehydes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 157573).—Alkyl formates react with 2 mols. of magnesium alkyl haloids to form secondary alcohols or their formic esters (Grignard, Abstr., 1901, i, 679). When, however, at least 2 mols. of alkyl formate are employed for each 2 mols. of magnesium alkyl or aryl haloid, aldehydes are obtained. For example, $\text{MgBrPh} + \text{H}\cdot\text{CO}_2\text{Et} = \text{OEt}\cdot\text{CHPh}\cdot\text{O}\cdot\text{MgBr}$. This intermediate compound either decomposes directly into benzaldehyde and $\text{MgBr}\cdot\text{OEt}$, or possibly reacts with water according to the equation: $\text{OEt}\cdot\text{CHPh}\cdot\text{O}\cdot\text{MgBr} + \text{H}_2\text{O} = \text{MgO} + \text{HBr} + \text{OEt}\cdot\text{CHPh}\cdot\text{OH}$, this alcoholate then decomposing into alcohol and benzaldehyde. In addition to the above example, the preparation of propaldehyde from ethyl iodide and amyl formate, of isovaleraldehyde from isoamyl bromide and ethyl formate, and of phenylacetaldehyde from benzyl chloride and methyl formate by means of the magnesium compounds is described.

C. H. D.

cycloButanone. NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 106—109).—*Tetramethylenecarboxylic bromamide*,



prepared by brominating tetramethylenecarboxylic acid and treating the bromo-anhydride thus obtained with ammonia, crystallises from aqueous alcohol in long, flat needles, melts at 153° , and dissolves readily in water or benzene.

cycloButanone, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{CO}$, obtained by the action of bromine and potassium hydroxide on the preceding bromide, has an odour resembling that of acetone, boils at $99\text{--}101^\circ$, has the sp. gr. 0.9344 at $18^\circ/18^\circ$, and n_D 1.4214 at 18° ; it is soluble in water, gives a crystalline compound with sodium hydrogen sulphite, and yields a *semicarbazone* separating from alcohol in plates melting at 221° . Oxidation with concentrated nitric acid gives succinic acid.

1:1-*Dibromocyclobutane*, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{CBr}_2$, boils at $159\text{--}161^\circ$ and has the sp. gr. 1.8934 at $20^\circ/20^\circ$; when treated with semicarbazide hydrochloride and potassium acetate, it is converted into the semicarbazone of cyclobutanone.

T. H. P.

Inversion of ψ -Ionone and its Derivatives. PAUL ALEXANDER (D.R.-P. 157647).—A certain quantity of resin is always formed in the inversion of ψ -ionone and its derivatives by acids. A better result

is obtained by heating the compound to be inverted with water or alcohol at 170—190°, with or without the addition of salts, such as the chlorides, acetates, or sulphates of the alkalis or alkaline earths.

ψ -Iononecarboxylic esters give an almost theoretical yield of ionone when heated with water under pressure; ψ -ionone gives a 50 per cent. yield of ionone with sodium acetate. In this case, it is advisable to separate the inverted product and repeat the operation, as ionone is less stable at high temperatures than ψ -ionone. C. H. D.

Formation of Additive Compounds from Hydroxylamine and Arylsulphonacetoneitriles. JULIUS TRÖGER and FRANZ VOLKMER (*J. pr. Chem.*, 1905, [ii], 71, 236—248. Compare foregoing abstract; Tiemann and Krüger, *Abstr.*, 1884, 1325; 1885, 790).—Arylsulphonacetoneitriles form amidoximes when warmed with hydroxylamine hydrochloride and sodium carbonate in concentrated aqueous-alcoholic solution.

Phenylsulphonethenylamidoxime, $\text{SO}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}\cdot\frac{1}{2}\text{H}_2\text{O}$ (or sometimes with H_2O), forms glistening, white prisms or leaflets, and melts at 158°. *p-Tolylsulphonethenylamidoxime* crystallises in white leaflets or needles and melts and decomposes at 190—192°. It may also be obtained in granular crystals, which sinter at 190° and melt and decompose at about 196°. *o-Tolylsulphonethenylamidoxime* forms a white powder and melts at about 104°. *1:3-Xylyl-4-sulphonacetoneitrile* melts at 79—80°. *1:3-Xylyl-4-sulphonethenylamidoxime* forms a white, woolly, crystalline mass and melts and decomposes at 142°. ψ -*Cumylsulphonacetoneitrile*, formed from sodium ψ -cumenesulphonate and chloroacetoneitrile, crystallises in long, glistening needles and melts at 110—111°. ψ -*Cumylsulphonethenylamidoxime* crystallises in glistening, white leaflets and melts at 146°. α -*Naphthylsulphonethenylamidoxime* forms small, glistening, granular crystals and melts and decomposes at about 206°. β -*Naphthylsulphonethenylamidoxime* crystallises in matted, glistening needles and melts and decomposes at 170—175°. *m-Phenylenedisulphondienylamidoxime* forms a white, crystalline powder and decomposes when strongly heated. *p-Chlorophenylsulphonethenylamidoxime* crystallises in glistening, white leaflets and melts and decomposes at 202°. *p-Bromophenylsulphonethenylamidoxime* crystallises in glistening, white leaflets and melts and decomposes at 198°. Potassium *p*-iodobenzenethiosulphonate, formed by the action of potassium sulphide on *p*-iodobenzenesulphonic chloride in warm concentrated aqueous solution, is converted by potassium cyanide in concentrated aqueous solution into potassium *p*-iodobenzenesulphiniate. *p*-Iodobenzenesulphinic acid melts at about 160° (compare *Abstr.*, 1902, i, 274). *p*-*Iodophenylsulphonethenylamidoxime* crystallises in white leaflets and melts and decomposes at 176°.

o-Anisolesulphonacetoneitrile, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CN}$, crystallises in glistening, white prisms, and melts at 84—85°. *o-Anisolesulphonethenylamidoxime* forms a white, crystalline powder and melts at 105°. *p-Anisolesulphonacetoneitrile* crystallises in colourless, glistening needles and melts at 115°. *p-Anisolesulphonethenylamidoxime* crystallises in stellate groups of slender needles and melts at 116°.

p-Phenetolesulphonacetoneitrile crystallises in needles and melts at

140—141°. *p*-Phenetolesulphonethenylamidoxime forms a white, crystalline powder and melts and decomposes at 175°. G. Y.

Ketonic Fission of Carbinols. GEORG VON GEORGIEVICS (*Ber.*, 1905, **38**, 884—886. Compare Fischer and Hess, this vol., i, 205).—Pararosaniline reacts with hydrogen peroxide in slightly alkaline solution to form 4:4'-diaminobenzophenone, which melts at 244° (m. p. 237°, Wichelhaus, *Abstr.*, 1889, 781). In the same manner, crystal-violet yields tetramethyldiaminobenzophenone, which melts at 175° (compare Fehrmann, *Abstr.*, 1888, 156; Graebe, *Abstr.*, 1888, 158). G. Y.

Condensation of Imines with Ketones and Nitromethane. CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], **33**, 395—399. Compare *Abstr.*, 1904, i, 832, and this vol., i, 214).—*Anilinophenylethyl isopropyl ketone*, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPr}^\beta$, obtained by the action of benzylideneaniline on methyl isopropyl ketone dissolved in alcohol, crystallises in brilliant needles, melts at 119—120°, and dissolves readily in benzene, ether, or boiling alcohol. *Anilinophenylethyl butyl ketone* crystallises in leaflets, melts at 80°, and when dissolved in acetic or sulphuric acid and the solution poured on ice furnishes *benzylidenemethyl butyl ketone*, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_4\text{H}_9$, which forms colourless lamellæ and melts at 40°. The products obtained by the condensation of benzylideneaniline with methyl *p*-tolyl and methyl *m*-tolyl ketones melt at 173° and 172° respectively, resemble anilinobenzylacetophenone in solubility (Tambor and Wilde, *Abstr.*, 1898, i, 313), and on solution in sulphuric acid furnish the corresponding ketones; the *cinnamenyl-m-tolyl ketone* so obtained, crystallises from methyl alcohol in slightly yellow prisms and melts at 73°. *Anilino benzyl-lævulic acid*, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, melts at 148°, is readily soluble in acetone, less so in alcohol, ether, and benzene, and on solution in sulphuric acid yields benzylidenelævulic acid (Erlenmeyer, *Abstr.*, 1904, i, 500). The ethyl ester of the imino-acid crystallises in needles, melts at 93—94°, and is hydrolysed by sulphuric acid to *ethyl benzylidenelævulate*, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which crystallises in silky needles and melts at 44—45° (compare Erdmann, *Abstr.*, 1890, 495).

Anilinophenyl nitroethane, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}_2$, obtained by the action of nitromethane on benzylideneaniline forms large, colourless rhombohedra, melts at 90°, is readily soluble in ether, benzene, and warm alcohol, and when warmed with hydrochloric acid yields aniline and β -nitrostyrene. A mixture of benzaldehyde, acetone, piperidine, and alcohol, after being left for 45 days, yielded dibenzylideneacetone.

The author's results show that in order that a ketone may condense with benzylideneaniline it must contain a methyl group and must not contain a quaternary carbon atom next the carbonyl group. Condensation as a rule does not occur between ketones and imines possessing stable hydrochlorides, for example, benzylidene-*p*-phenetidine. Methyl cyanide and quinaldine do not condense with imines, in spite of their analogy with the methyl ketones. T. A. H.

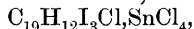
Dibenzylideneacetone and Triphenylmethane. VIII. ADOLF BAEYER [in part with RICHARD HALLENSLEBEN] (*Ber.*, 1905, **38**, 1156—1164. Compare *Abstr.*, 1903, i, 811; 1904, i, 308 and 898; this vol., i, 281).—*p*-Tri-iodotriphenylcarbinol, when purified by removing the azo-compounds which contaminate it by means of alcoholic-etheral stannous chloride, is quite colourless and melts at 162—163°.

When concentrated sulphuric acid is mixed with a solution of *p*-trichlorotriphenylcarbinol in chloral and chloroform is then added, the *sulphate*, $C_{19}H_{12}Cl_3 \cdot SO_4H, H_2SO_4$, separates in brown prisms or needles with a greenish-blue surface lustre. The *sulphate*,



of *p*-tri-iodotriphenylcarbinol is obtained in a similar manner and forms microscopic, brown crystals. The production of diacid salts from these weak bases is probably due to the employment of the concentrated sulphuric acid, which, it is suggested, consists of a dimolecularly associated acid, "dimolsulphuric acid."

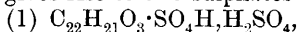
p-Trichlorotriphenylcarbinyl chloride gives with stannic chloride in chloroform solution the *stannichloride*, $C_{19}H_{12}Cl_4, SnCl_4$, which forms red crystals with a blue surface colour; the *stannichloride*,



derived from *p*-tri-iodotriphenylcarbinyl chloride, is a crimson, crystalline powder with a green, metallic lustre.

p-Trichlorotriphenylcarbinyl ethyl ether, $C_{21}H_{17}OCl_3$, crystallises from chloroform on adding alcohol in lustrous prisms and melts at 182°; *p*-tri-iodotriphenylcarbinyl ethyl ether forms small, white prisms and melts at 223°.

p-Trianisylcarbinol gives rise to two sulphates :



obtained by means of chloral and precipitating with ethyl acetate, forms orange-yellow needles; (2) $(C_{22}H_{21}O_3 \cdot SO_4H)_2, H_2SO_4$, probably a mixture of $C_{22}H_{21}O_3 \cdot SO_4H$ and $C_{22}H_{21}O_3 \cdot SO_4H, H_2SO_4$ obtained by adding sulphuric acid mixed with chloroform to a solution of the carbinol in chloroform, forms crimson crystals.

m-Trianisylcarbinol gives only the salt $(C_{22}H_{21}O_3 \cdot SO_4H)_2, H_2SO_4$ when sulphuric acid is mixed with its solution in chloral, ethyl acetate being subsequently added.

The colour of some triphenylcarbinol salts is discussed from the standpoint of the "carbonium" theory and of "halochromy."

W. A. D.

Action of Organo-magnesium Compounds on Cinnamylideneacetophenone. ELMER P. KOHLER (*Ber.*, 1905, **38**, 1203—1208. Compare this vol., i, 207, 208, 215).—*β*-Phenyl-*β*-styrylpropiofenone (*γ*-benzylidene-*β*-phenylbutyrophenone), $COPh \cdot CH_2 \cdot CHPh \cdot CH : CHPh$, prepared by the action of magnesium phenyl bromide on cinnamylideneacetophenone, melts at 93°. Its solution in concentrated sulphuric acid is intensely red. Its constitution was determined by the isolation of benzoic acid and *β*-benzoyl-*α*-phenylpropionic acid as products of its oxidation by potassium permanganate. Its *oxime* separates from alcohol in needles and melts at 129°; its *dibromide*

separates from a mixture of chloroform and light petroleum in glistening prisms and melts at 171° .

β -Benzyl- β -styrylpropiofenone (γ -benzylidene- β -benzylbutyrophenone), $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CH}\cdot\text{CHPh}$, prepared by the action of magnesium benzyl chloride on cinnamylideneacetophenone, melts at 125° . That the substance is a ketone and not a tertiary alcohol, as indicated by Bauer, was proved by the formation of benzoic acid and β -benzoyl α -benzylpropionic acid as its oxidation products. *β -Benzoyl- α -benzylpropionic acid*, $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$, separates from alcohol in needles and melts at 176° .

β -Benzyl- β -styrylpropiofenone dibromide separates from a mixture of alcohol and chloroform in glistening prisms and melts at 152° .

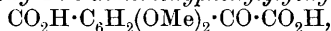
β -Benzyl- β -styrylpropiofenone oxime separates from a mixture of ether and light petroleum in needles and melts at 144° .

β -Styryl- β -ethylpropiofenone (γ -benzylidene- β -ethylbutyrophenone), $\text{COPh}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CH}\cdot\text{CHPh}$, prepared by the action of magnesium ethyl bromide on cinnamylideneacetophenone, is identical with the product described by Bauer as "diphenylmethylhexadienol," but is not a tertiary alcohol, since it yields benzoic acid and β -benzoyl- α -ethylpropionic acid on oxidation. Its *dibromide* separates from a mixture of alcohol and chloroform in prisms and melts at 142° . Its *oxime* separates from light petroleum in needles and melts at 91° .

A. McK.

Action of Zinc Chloride on Acid Esters of Phenols. II.

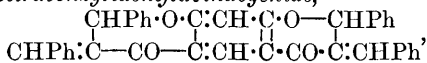
2:4-Dihydroxy-1:5-diacetylbenzene. JOHAN F. EIJKMAN, F. BERGEMA, and I. T. HENRARD (*Chem. Centr.*, 1905, i, 814—817; from *Chem. Weekblad*, 2, 59—72 and 79—93. Compare Abstr., 1904, i, 664).—2:4-Dihydroxy-1:5-diacetylbenzene is best prepared by warming resorcinol diacetate with zinc chloride; it forms colourless needles melting at 183° (corr.), sparingly soluble in cold, more readily in warm organic solvents, and is identical with the "*isoresacetophenone*" of Claus and Huth (Abstr., 1896, i, 227). By the action of alkyl iodides or bromides on the potassium salt, simple and mixed ethers are formed. Those of the type $\text{C}_6\text{H}_2\text{Ac}_2(\text{OR}^1)(\text{OR}^{11})$ are identical independently of the order of introduction of the groups R^1 and R^{11} , thus proving the orientation of the parent substance. The dioximes of the ethers as a rule crystallise from alcohol or benzene in slender needles. 2:4-Dihydroxy-1:5-diacetylbenzene *dioxime* melts at 242° . An excess of potassium permanganate oxidises the dimethyl and diethyl esters of 2:4-dihydroxy-1:5-diacetylbenzene to 4:6-dimethoxy- and 4:6-diethoxy-isophthalic acids, separating from alcohol in crystals, sparingly soluble in water, and melting and decomposing at 266° and 250° respectively. The dimethyl ether with seven atomic proportions of oxygen gives 3-carboxy-4:6-dimethoxyphenylglyoxylic acid,



as colourless needles melting and decomposing at 243° .

2:4-Dihydroxy-1:5-diacetylbenzene condenses with benzaldehyde, yielding the *monobenzylidene* derivative, which forms bright yellow needles melting at 192° , and the *dibenzylidene* derivative, which crystallises from benzene in reddish-yellow needles and melts at 202° ,

whilst with anisaldehyde the corresponding *dianisylidene* compound, which separates from benzene in golden-yellow needles and melts at 204° , is produced. By the action of benzaldehyde and hydrogen chloride on the solution of the dibenzylidene compound in alcohol and a little benzene, *tetrabenzylideneflavindogenide*,



is obtained; it separates from benzene in yellow crystals, melts at 257° , and dissolves in boiling dilute alkalis to a yellow, and in sulphuric acid to a cherry-red, solution.

The constants of the following *ethers* of 2:4 dihydroxy-1:5-acetylbenzene and their oximes are given, the melting points being corrected: *monomethyl*, m. p. 121.5° , sp. gr. 1.1297, and $n_D 1.52932$ at 134.7° ; *oxime*, m. p. 274° ; *monoethyl*, m. p. 109° , sp. gr. 1.1120, and $n_D 1.52876$ at 109.1° ; *oxime*, m. p. 217° ; *monopropyl*, m. p. 94.5° , sp. gr. 1.0821, and $n_D 1.51989$ at 112.4° ; *oxime*, m. p. 186° ; *monoisopropyl*, m. p. 97.5° ; *oxime*, m. p. 162° ; *monobutyl*, m. p. 63° , sp. gr. 1.0860, and $n_D 1.52690$ at 78.8° ; *oxime*, m. p. 170° ; *monoisobutyl*, m. p. 88° ; *oxime*, m. p. 213° ; *dimethyl*, m. p. 171.5° ; *oxime*, m. p. 255° ; *diethyl*, m. p. 156° ; *oxime*, m. p. 245° ; *dipropyl*, m. p. 86° , sp. gr. 1.0173, and $n_D 1.50150$ at 131.1° ; *oxime*, m. p. 206° ; *diisopropyl*, m. p. 126.5° ; *oxime*, m. p. 235° ; *dibutyl*, m. p. 92.5° , sp. gr. 0.9893, and $n_D 1.49324$ at 110.8° ; *oxime*, m. p. 169° ; *diisobutyl*, m. p. 99° ; *oxime*, m. p. 207° ; *methylethyl*, m. p. 152° ; *oxime*, m. p. 241° ; *methylpropyl*, m. p. 125.5° ; *oxime*, m. p. 237° ; *methylisopropyl*, m. p. 97° ; *oxime*, m. p. 235° ; *methylbutyl*, m. p. 117° ; *oxime*, m. p. 189° ; *methylisobutyl*, m. p. 102.5° ; *oxime*, m. p. 210° ; *ethylpropyl*, m. p. 95° ; *oxime*, m. p. 218° ; *ethylisopropyl*, m. p. 101.5° ; *oxime*, m. p. 235° ; *ethylbutyl*, m. p. 104° ; *oxime*, m. p. 193° ; *ethylisobutyl*, m. p. 72° ; *oxime*, 195° ; *propylisopropyl*, m. p. 78° ; *oxime*, m. p. 220° ; *propylbutyl*, m. p. 61.5° ; *oxime*, m. p. 176° ; *propylisobutyl*, m. p. 64° ; *oxime*, m. p. 200° ; *isopropylbutyl*, m. p. 76° ; *oxime*, m. p. 196° ; *isopropylisobutyl*, m. p. 80° ; *oxime*, m. p. 211° ; *butylisobutyl*, m. p. 78° ; *oxime*, m. p. 187° .

2:4-Dihydroxy-1 acetylbenzene has a sp. gr. 1.1800 and $n_D 1.56467$ at 141.1° ; the following constants for some of its ethers are given: 4-methyl, m. p. 50° , sp. gr. 1.1310, and $n_D 1.54322$ at 81.2° ; 4-ethyl, m. p. 48° , sp. gr. 1.0866, and $n_D 1.53082$ at 80° ; 4-propyl, m. p. 25° , sp. gr. 1.0553, and $n_D 1.52128$ at 80.1° ; 4-butyl, m. p. 42° , sp. gr. 1.0333, and $n_D 1.51479$ at 79.7° ; dimethyl, m. p. 40° , sp. gr. 1.0914, and $n_D 1.52476$ at 80.1° ; diethyl, m. p. 68° , sp. gr. 1.0266, and $n_D 1.50627$ at 80.7° ; dipropyl, m. p. 26° , sp. gr. 0.9928, and $n_D 1.49758$ at 79.5° ; dibutyl, m. p. 32° , sp. gr. 0.9678, and $n_D 1.49029$ at 80° ; 4-ethyl-2-methyl, m. p. 44° , sp. gr. 1.0562, and $n_D 1.51587$ at 79.1° ; 4-methyl-2-ethyl, m. p. 67.5° , sp. gr. 1.0571, and $n_D 1.51434$ at 80.2° .

The preparation and constants of some ketones are also given: *o-methylacetophenone*, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{Me}$, from calcium *o*-toluate and calcium acetate, is a liquid boiling at 79° , 108° , and 214° under 5, 30, and 761 mm. pressure respectively; *p-methylacetophenone*, from toluene, acetyl chloride, and aluminium chloride, boils at 228° under 759 mm. pressure; *m-hydroxyacetophenone*, from *m*-nitroacetophenone, boils at 153° and 296° under 5 and 756 mm. pressure respectively, the *methyl*

ether boiling at 99°, 152°, and 252° under 4, 38, and 760 mm. pressure respectively; *p*-hydroxyacetophenone, from phenol, acetyl chloride, and zinc chloride, melts at 107°, the methyl ether, from anisole, acetyl chloride, and aluminium chloride, melting at 35°. The optical constants are given for the following.

o-Hydroxybenzaldehyde, sp. gr. 1.1589 and n_D 1.56422 at 21.3°; *p*-hydroxybenzaldehyde, sp. gr. 1.1291 and n_D 1.57055 at 130°; *o*-methylacetophenone, sp. gr. 1.0010 and n_D 1.52415 at 16.8°; *p*-methylacetophenone, sp. gr. 1.0029 and n_D 1.52827 at 22°; *p*-tolyl pentadecyl ketone, sp. gr. 0.8665 and n_D 1.46954 at 77.3°; *p*-tolyl heptadecyl ketone, sp. gr. 0.8621 and n_D 1.46799 at 78°; *p*-anisyl pentadecyl ketone, sp. gr. 0.8981 and n_D 1.47605 at 80.5°; *o*-hydroxyacetophenone, sp. gr. 1.1302 and n_D 1.55405 at 18.2°; *o*-ethoxyacetophenone, sp. gr. 1.0036 and n_D 1.49684 at 78.3°; *m*-hydroxyacetophenone, sp. gr. 1.0992 and n_D 1.53482 at 109.2°; *m*-methoxyacetophenone, sp. gr. 1.0943 and n_D 1.53665 at 19°; *p*-hydroxyacetophenone, sp. gr. 1.1090 and n_D 1.55773 at 109.2°; *p*-methoxyacetophenone, sp. gr. 1.0493 and n_D 1.52395 at 79.9°; *p*-acetyl-*m*-hydroxytoluene, sp. gr. 1.0592 and n_D 1.53689 at 135.3°. G. D. L.

Quinonoid Derivatives of Diphenyl. II. RICHARD WILLSTÄTTER and LUDWIG KALB (*Ber.*, 1905, **38**, 1232—1241. Compare Abstr., 1904, i, 1050).—*Diphenoquinone*, $C_{12}H_8O_2$, prepared by shaking diphenol dissolved in ether with lead peroxide for a day and subsequently, after decanting the ether, boiling the residue with benzene for a short time, is obtained either in hard, glistening, blue or brownish-red needles or in soft golden-yellow to bronze, minute needles. The first form is converted into the second on adding a trace of diphenol to the hot saturated solution or by precipitating the benzene solution with light petroleum. On heating, it decomposes at about 165°.

Diphenoquinhydrone, $C_{24}H_{18}O_4$, is best prepared by mixing molecular quantities of diphenoquinone in benzene and diphenol dissolved in ether; it crystallises in dark green needles, which decompose at 180°, and forms a violet-coloured sodium salt.

By the oxidation of benzidine with lead peroxide, a compound, $C_{12}H_{10}N_2$, is obtained, probably the *di-imine* of diphenoquinone. This crystallises from benzene in well-formed, long, reddish-brown needles pointed at both ends, melts at 285—286°, and dissolves in concentrated sulphuric acid with a blood-orange-red coloration. E. F. A.

Disulphonic Acids of Anthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 157123).—When the sulphonation of anthraquinone in the presence of a mercury salt (Abstr., 1904, i, 513) is carried out at a higher temperature or for a longer time, or if a larger quantity of sulphur trioxide is used, the product is a mixture of anthraquinone-1:5- and -1:8-disulphonic acids, which is readily separated into its components. Sulphonation in the β -position does not take place, as in the ordinary process of sulphonation of anthraquinone. C. H. D.

Nitro-derivatives of Alkylaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 156759).—The secondary and tertiary alkyl derivatives of aminoanthraquinones and their

sulphonic acids (Abstr., 1903, i, 498, 839), unlike the parent amino-compounds, are readily nitrated by means of nitric and sulphuric acids. In the case of tertiary alkyl derivatives, one alkyl group is often eliminated, secondary alkyl derivatives being obtained. The nitro-group in the derivatives thus prepared is readily exchanged for arylamino-residues.

4-Nitro-1-methylaminoanthraquinone, prepared by nitrating α -methylaminoanthraquinone, crystallises from pyridine in long, glistening, reddish-brown needles and melts at 250° . It dissolves sparingly in alcohol or acetic acid, more readily in acetone, and is insoluble in dilute hydrochloric acid. 2-Nitro-1-methylaminoanthraquinone is formed at the same time, and may be separated by its greater solubility in organic solvents.

4:8-Dinitro-1:5-dimethylaminoanthraquinone separates from pyridine in dark violet crystals and dissolves in pyridine to a bluish-red solution and in concentrated sulphuric acid to a yellow solution. The *nitrate* is colourless.

The colour-reactions of many similar derivatives are described.

C. H. D.

Methyl Ethers of Hydroxyanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 156762).—The α -sulphonic acids of anthraquinone react with methyl alcohol and sodium hydroxide on warming, the sulpho-group being replaced by the methoxy-group. Thus anthraquinone- α -sulphonic acid yields erythroxyanthraquinone methyl ether; anthraquinone-1:8-disulphonic acid yields chrysazin dimethyl ether, and anthraquinone-1:5-disulphonic acid yields anthrafin dimethyl ether.

C. H. D.

Action of Alcoholic Potassium Hydroxide on Phenanthraquinone. RICHARD MEYER and OSKAR SPENGLER (*Ber.*, 1905, 38, 950—953).—The decomposition of the lactone, $C_{16}H_{10}O_4$, (this vol., i, 219), on melting is shown by an analysis of the gaseous products to take place quantitatively according to the equation $2C_{16}H_{10}O_3 = C_{29}H_{16}O_2 + CO_2 + 2CO$, the solid product being solely *didiphenylene-pyrone*, $\begin{array}{c} C_6H_4 \cdot C \cdot CO \cdot C \cdot C_6H_4 \\ | \quad | \\ C_6H_4 \cdot C - O - C \cdot C_6H_4 \end{array}$, which is obtained colourless after repeated crystallisations. The formation of a six-membered ring from the coalescence of two five-membered rings is remarkable in view of Baeyer's tension theory.

W. A. D.

Oxidation of *iso*Borneol to Camphor. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 157590).—The yield of camphor obtained by oxidising *isoborneol* with potassium permanganate in acetic acid solution (Semmler, Abstr., 1900, i, 351) does not exceed ten per cent., but may be greatly increased by adding the *isoborneol* in powdered form, or dissolved in benzene or light petroleum, to an aqueous solution of permanganate, and agitating thoroughly.

C. H. D.

[Cinnamylidenecamphor and its Reduction Products.] HANS RUPE and GUNNAR FRISSELL (*Ber.*, 1905, 38, 1171).—A reply to Bruhl's

suggestion (this vol., i, 293) that inaccurate measurements of molecular refractions were made in a former paper (this vol., i, 220).

W. A. D.

Menthone derived from Hexahydrothymol. LÉON BRUNEL (*Compt. rend.*, 1905, 140, 792—794).—The two isomeric thymomenthols (hexahydrothymols; compare this vol., i, 197) obtained by direct reduction of thymol yield thymomenthone, $C_{10}H_{18}O$, when oxidised with chromic acid in acetic acid solution at about 0° .

Thymomenthone is a colourless, mobile liquid with an odour and taste resembling those of ordinary menthone. It boils at 212° under 760 mm., has a sp. gr. 0.911 at 0° , and does not crystallise when cooled to -10° . When reduced by sodium in alcoholic solution, or by hydrogen in presence of finely-divided nickel, it forms β -thymomenthol. *Thymomenthonesemicarbazone* forms colourless, odourless crystals melting at 159° . *Thymomenthoneoxime* forms small, colourless needles melting at 80° . When the oxime is reduced by sodium in alcoholic solution, *thymomenthylamine* is obtained as a colourless liquid with a disagreeable odour, which boils at 208° under 760 mm., absorbs carbon dioxide from the air, and forms well-defined salts with acids. The *picate* forms yellow needles, which are only slightly soluble in water and alcohol, and melts at 168 — 169° .

H. M. D.

Coagulation and Solubility of Caoutchouc. CARL OTTO WEBER (*Chem. Centr.*, 1905, i, 886; from *Gummi-Zeit.*, 19, 354—356. Compare Abstr., 1904, i, 331).—The product obtained from caoutchouc milk by purely mechanical means, such as by centrifugal separation, for example, is termed “coalesced” caoutchouc in order to distinguish it from coagulated caoutchouc. These products have different physical properties, and are probably different polymerides. Since the caoutchouc molecule contains at least two, and probably three, double bonds for each $C_{10}H_{16}$ group, polymerisation cannot have affected the number of these bonds. The solubility even of the best kinds of crude Para caoutchouc has been found to vary within very great limits, and the author's previous statement that highly polymerised caoutchouc is insoluble in ether applies only to the particular kind of caoutchouc examined (fine cut sheet). The variations of solubility are so great that it is impossible to regard any solvent as the best. The portion which is soluble in ether can be isolated from carefully selected crude materials in the form of a hydrocarbon, $C_{10}H_{16}$. Fractional separation by means of other solvents always yields products which contain oxygen, the percentage of this element increasing slowly from fraction to fraction. The quantity of oxygen contained in the insoluble substance is greater the less the proportion of this substance contained in the original material. Fendler's results (*Gummi-Zeit.*, 19, 41) only show that the amount of insoluble substance varies within extremely wide limits. The quality of caoutchouc is, doubtless, to some extent dependent on the insoluble portion, for in the process of milling this substance practically disappears.

E. W. W.

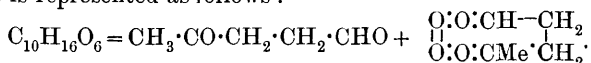
Caoutchouc. Decomposition and Constitution of Para Caoutchouc. CARL D. HARRIES (*Ber.*, 1905, **38**, 1195—1203. Compare Abstr., 1904, i, 757).—A current of ozonised oxygen, containing 5.5—6 per cent. of ozone, was passed into a cooled solution of Para caoutchouc in chloroform, and when the product had been concentrated under diminished pressure, a mixture of ethyl acetate and light petroleum was added. *Caoutchouc ozonide*, $C_{10}H_{16}O_6$, separated as an oil, which solidified to a glassy mass and melted at about 50° ; it is explosive. When water was added and the product then submitted to distillation in a current of steam, lævulic aldehyde passed over. The distillate reduced Fehling's solution, gave an intense pyrrole reaction, and with phenylhydrazine acetate formed phenylmethyldihydropyridazine, melting at 197° and identical with the product directly obtainable from lævulic aldehyde. The presence of the latter in the distillate was further proved by the formation of its dioxime, and by its isolation. Lævulic aldehyde has the sp. gr. 1.016 at 21.5° and n_D 1.42695 at 21.5° .

When the ozonide is distilled with steam until the distillate ceases to give the pyrrole reaction, the residue contains lævulic acid.

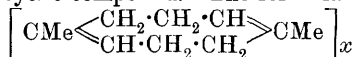
When the action of steam on the ozonide is carried out for a short time only, *lævulic aldehyde peroxide*, melting and decomposing at 197° , separates. It crystallises from water in leaflets and is readily converted by steam into lævulic aldehyde. It liberates iodine from potassium iodide, decolorises potassium permanganate and indigo solutions, reduces ammoniacal silver nitrate, and deflagrates when quickly heated.

No other volatile aldehydes or ketones result as products of the decomposition of the ozonide. The products obtained are readily estimated quantitatively.

The decomposition of the ozonide into lævulic aldehyde and its peroxide is represented as follows:



Caoutchouc is a cyclic compound. The formula



may provisionally be assigned to it. Caoutchouc is optically inactive.

A. McK.

Aucubin, the Glucoside of Aucuba Japonica. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Ann. Chim. Phys.*, 1905, [viii], **4**, 289—318).—A *résumé* of work already published (compare Abstr., 1902, i, 634; ii, 55; 1904, i, 606). Crystalline hydrated aucubin has $[\alpha]_D -164.9^\circ$, whilst the anhydrous compound has $[\alpha]_D -174.4^\circ$.

M. A. W.

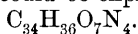
Digitonin. HEINRICH KILIANI (*Arch. Pharm.*, 1905, **243**, 5—12).—A reply to Cloetta (*Arch. exp. Path. Pharm.*, 1901, **45**, 435; also 1898, **41**, 421). Cloetta's "amorphous digitonin" is certainly a mixture, and so simple a formula for it as $C_{28}H_{47}O_{14}$ is out of the question.

C. F. B.

Preparation of a Non-poisonous Saponin. FIRMA EMANUEL MERCK (D.R.-P. 156954).—The saponin extracted from the leaves, bark, and other portions of *Bulnesia Sarmienti* or *Guaiacum officinale* by means of benzene, and purified by means of lead acetate, is neutral and non-poisonous, and does not exert a solvent action on red blood-corpuscles. Its formula is $C_{22}H_{36}O_{10}$, and it appears to be a methyl derivative of saponic acid, $C_{21}H_{34}O_{10}$. It dissolves readily in water or alcohol, and is precipitated by ether as a dull yellow powder.

C. H. D.

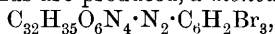
Bilirubin, the Red Colouring Matter of the Bile. WILLIAM R. ORNDORFF and JOHN E. TEEPLE (*Amer. Chem. J.*, 1905, **32**, 215—250).—In a previous paper (Abstr., 1901, i, 602), it was shown that bilirubin does not contain alkoxy-groups, but has one alkyl group attached to nitrogen, and is probably a pyrrole derivative; analysis showed that its composition could be expressed by the formula



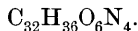
Küster (Abstr., 1902, i, 388) has demonstrated that the material used in this investigation was a mixture of two substances which differ in composition and solubility in chloroform.

It is now found that pure crystalline bilirubin has the composition $(C_{16}H_{18}O_3N_2)_x$ and crystallises from chloroform in monoclinic or triclinic prisms; its solubility cannot be determined with accuracy on account of its tendency to form supersaturated solutions. On reduction with zinc dust or nascent hydrogen iodide, it is converted into hæmopyrrole.

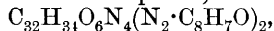
By the action of tribromobenzenediazonium hydrogen sulphate on bilirubin, two compounds are produced, a *monoazo*-derivative,



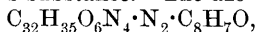
and a *bisazo*-derivative, $C_{32}H_{34}O_6N_4(N_2 \cdot C_6H_2Br_3)_2$. These products are easily distinguishable, as the former gives a red and the latter a purple colour with potassium hydroxide. Determinations of the molecular weight of the bisazo-compound in chloroform or ethyl acetate solution by the ebullioscopic method confirm the above formula, whence it must be concluded that bilirubin has the formula



On repeating the work of Pröscher (Abstr., 1900, i, 571), it has been found that acetophenonediazonium chloride combines with bilirubin forming both *azo*- and *bisazo*-derivatives, which are best separated by means of carbon disulphide; the latter compound,



crystallises in long, wedge-shaped plates of the triclinic system and is identical with Pröscher's substance. The *azo*-compound,



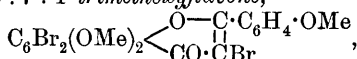
is insoluble in carbon disulphide and only slightly soluble in chloroform. All these *azo*-derivatives of bilirubin show characteristic absorption bands which are fully described.

E. G.

Tannins producing a "Bloom" [on Leather]. M. NIERENSTEIN (*Chem. Centr.*, 1905, i, 701; from *Collegium*, 1905, 21—23).—Pyro-

gallol tannins give a "bloom" of ellagic acid on leather, the acid being formed either by synthesis from gallic esters or by decomposition of ellagic glucosides already existing in the tannin. Myrobalans yielded ellagic acid on extraction with hot water and crystallisation. *Tetra-acetyllellagic acid*, $C_{22}H_{16}O_{12}$, melts at $276-279^{\circ}$ and, on warming with concentrated sulphuric acid, gives colourless ellagic acid, which is not coloured by nitric acid. The original mother liquor, after warming with dilute sulphuric acid, yields gallic acid on extraction with ether and pyrogallol on subsequent extraction with ethyl acetate. Dextrose is present in the aqueous residue. G. D. L.

A Second Synthesis of Apigenin. MARIE BREGER and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 931—933).—5 : 7 : 4'-Trimethoxyflavanone (Kostanecki, Lampe, and Tambor, *Abstr.*, 1904, i, 441) reacts with a chloroform solution of bromine yielding 3 : 6 : 8-*tribromo-5 : 7 : 4' - trimethoxyflavanone*, $C_6Br_2(OMe)_2$ $\begin{matrix} \text{O}-CH\cdot C_6H_4\cdot OMe \\ | \\ CO\cdot CHBr \end{matrix}$, which melts and decomposes at 145° . Alcoholic potash converts this into 6 : 8-*dibromo-5 : 7 : 4' - trimethoxyflavone*,



which crystallises in needles melting at 245° . When boiled with concentrated hydriodic acid for several hours, it yields 5 : 7 : 4'-*trihydroxyflavone* (Czajkowski, Kostanecki, and Tambor, *Abstr.*, 1900, i, 504). J. J. S.

3'-Hydroxyflavonol. A. GUTZEIT and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 933—935. Compare Kostanecki and Lampe, *Abstr.*, 1904, i, 440; Kostanecki and Stoppani, *ibid.*, 443).—*o*-Hydroxyacetophenone condenses with *m*-methoxybenzaldehyde yielding 2'-*hydroxy-3-methoxychalkone*, $OH\cdot C_6H_4\cdot CO\cdot CH\cdot CH\cdot C_6H_4\cdot OMe$, which crystallises from alcohol in yellow plates melting at $94-95^{\circ}$ and soluble in concentrated sulphuric acid. When boiled with an aqueous alcoholic solution of sulphuric acid, it yields 3'-*methoxyflavanone*, which crystallises in colourless prisms melting at $77-78^{\circ}$. 3-*isoNitroso-3'-methoxyflavanone*, $C_6H_4 \begin{matrix} \text{O}-CH\cdot C_6H_4\cdot OMe \\ | \\ CO\cdot C\cdot N\cdot OH \end{matrix}$, crystallises from benzene in colourless needles, melts and decomposes at $159-160^{\circ}$, and when boiled with a mixture of acetic and 10 per cent. sulphuric acid yields 3'-*methoxyflavonol*, $C_6H_4 \begin{matrix} \text{O}-C\cdot C_6H_4\cdot OMe \\ | \\ CO\cdot C\cdot OH \end{matrix}$, which crystallises from alcohol in pale yellow plates melting at 134° . Its solution in concentrated sulphuric acid is pale greenish-yellow, and when warmed with sodium hydroxide it yields a sparingly soluble *sodium* derivative with an intense yellow colour. The *acetyl* derivative melts at $117-118^{\circ}$. The methoxy-compound when hydrolysed with concentrated hydriodic acid, yields 3'-*hydroxyflavonol*, $C_{15}H_{10}O_4$, in the form of pale yellow needles melting at 237° ; the *acetyl* derivative melts at 166° . J. J. S.

An Isomeride of Quercitol. STANISLAUS VON KOSTANECKI and FR. RUDSE (*Ber.*, 1905, **38**, 935—938).—Gallacetophenone dimethyl ether condenses with veratraldehyde yielding 2'-hydroxy-3':4':3:4-tetramethoxychalkone, $\text{OH} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, in the form of yellow needles melting at 124° and soluble in concentrated sulphuric acid to a reddish-yellow solution; the *acetyl* derivative melts at 119° . When boiled with alcohol and dilute hydrochloric acid, it yields 7:8:3':4'-tetramethoxyflavanone, $\text{C}_{19}\text{H}_{20}\text{O}_6$, which crystallises from carbon disulphide in colourless, glistening needles melting at 144° . The *isonitroso*-derivative forms pale yellow needles melting and decomposing at 172° and soluble in sodium hydroxide solution; when heated with acetic and dilute sulphuric acids, it yields 7:8:3:4-tetramethoxyflavonol, $\text{C}_{19}\text{H}_{18}\text{O}_7$, in the form of pale yellow needles melting at 217° . The *acetyl* derivative melts at 176° .

Concentrated hydriodic acid hydrolyses the tetramethyl ether to 7:8:3':4'-tetrahydroxyflavonol, $\text{C}_{15}\text{H}_{10}\text{O}_7 \cdot 7\text{H}_2\text{O}$, a compound closely resembling fisetin. It melts and decomposes at 308° and is a good dye for mordanted fibres. It dissolves in dilute alkalis yielding reddish-yellow solutions and yields a *penta-acetyl* derivative melting at 172 — 173° .

J. J. S.

Influence of Light and Heat on the Chlorination and Bromination of Homologues of Thiophen. ST. OPOLSKI (*Bull. Acad. Sci. Cracow*, 1904, 727—732).—Chlorination and bromination of 2-methyl- or 2-ethyl-thiophen in sunlight results almost exclusively in the substitution of halogen in the ring, only very small quantities of halogen entering the side-chain. The bromination was effected by means of bromine vapour in a current of carbon dioxide, and in the case of 2-methylthiophen resulted in the formation of *bromo-2-methylthiophen*, which forms a liquid of pleasant odour, boiling at 177° (corr.) under 740 mm. pressure and having a sp. gr. 1.5529 at $20^\circ/4^\circ$ and n_D 1.5673. It gives an emerald-green coloration with phenanthraquinone and sulphuric acid in acetic acid solution, and an olive-violet indophenin reaction. The solid products of bromination are tribromo-2-methylthiophen and a *dibromo-2-methylthiophen*, which forms colourless needles, melts at 44 — 45° , and is readily soluble in warm alcohol or ether. When boiling 2-methylthiophen is brominated, the same products are formed, but there is considerable charring.

Under similar conditions, chlorination leads to the production mainly of *chloro-2-methylthiophen*, which boils at 153.7° (corr.) under 738 mm. pressure, has a sp. gr. 1.2016 at $17^\circ/4^\circ$, n_D 1.5367, and gives a yellowish-green Laubenheimer reaction, the violet indophenin colour being produced with greater difficulty.

Bromination of 2-ethylthiophen leads to the formation of the known bromo-2-ethylthiophen, which boils at 90 — 100° under 30—40 mm. pressure, has a sp. gr. 1.4642 at $20^\circ/4^\circ$, and n_D 1.5576 at 20° .

G. D. L.

Alkine Esters of Hydroxy-acids. CHININFABRIK BRAUNSCHWEIG; BUCHLER & Co. (D.R.-P. 157693).—It is not possible to condense fatty

hydroxyacyl chlorides with alkynes, internal condensation taking place. Esters containing an acyloxy-group, however (Abstr., 1904, i, 685), react readily, and the acyl group may then be removed by hydrolysis with acids. The preparation of inactive atropine from acetyltropyltropine, of tropyl-lupineine from acetyltropyl-lupineine, and of salicyltropine from acetylsalicyltropine, is described. C. H. D.

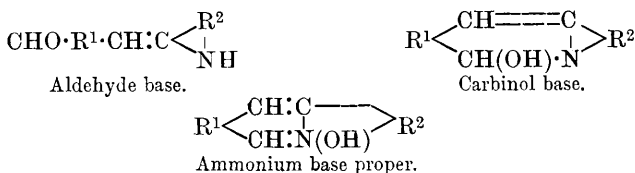
Alkaloid from Papaver Dubium. VITTORIO PAVESI (*Chem. Centr.*, 1905, i, 826—827; from *Rend. R. Ist. Lomb. sci. lett.*, [ii], 38, 117—121).—By extraction of the seed capsules of *Papaver dubium* with light petroleum, a previously unknown alkaloid, *aporeine*, is obtained. The thick, yellow, amorphous extractive product, amounting to 0.015 per cent., yields with 10 per cent. hydrochloric acid the *hydrochloride*, which forms glistening scales melting at about 230°, and gives precipitates with silver nitrate and phosphomolybdic acid. The base forms microscopic leaflets after crystallisation from ether, light petroleum, or chloroform. When a solution of a trace of the alkaloid or its hydrochloride in a drop of nitric acid of sp. gr. 1.3 is dropped into concentrated sulphuric acid, a violet, brown, and finally yellow coloration is produced, a similar result being given by the base with strong sulphuric acid in which a crystal of potassium chlorate has been dissolved. The hydrochloride gives a greyish-blue, green, brown, and finally yellow coloration with Fröhde's reagent; a green, blue, and finally black coloration with a solution of 2 or 3 drops of 40 per cent. formalin in 3 c.c. of concentrated sulphuric acid; with strong sulphuric acid, especially in the presence of potassium nitrate, or with fuming nitric and sulphuric acids in the presence of potassium dichromate, a brown coloration.

The hydrochloride produces on the tongue at first a burning and then a numbing sensation. The alkaloid is a tetanus poison similar to thebaine. G. D. L.

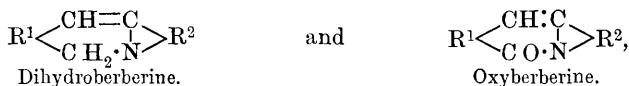
Constitution of ψ -Ammonium Bases with reference to the Alkaloids and the Products these yield by Transformation. JOHANNES GADAMER (*Arch. Pharm.*, 1905, 243, 12—29. Compare Decker, Abstr., 1902, i, 691).—A theoretical paper introductory to those following it (see next abstract and this vol., i, p. 353). The author considers that the ψ -ammonium bases exhibit a peculiar kind of tautomerism, such as renders possible the existence of three isomerides, one of which, however, may sometimes be too unstable to form derivatives. The relationship between these tautomeric forms is indicated by the following atomic groupings: (1) ammonium base proper, $\cdot\text{NMe}(\text{OH})\cdot\text{CH}\cdot$; (2) carbinol base, $\cdot\text{NMe}\cdot\text{CH}(\text{OH})\cdot$; (3) aldehyde (or ketone) base, $\cdot\text{NHMe}$ with $\cdot\text{CHO}$. It will be seen that the formation of the last form involves the breaking of a bond within the formula of the molecule, and consequently a lessening of the number of rings present.

The triphenylmethane dyes form a special group of ψ -bases, in which the structure of the molecule excludes the possibility of an aldehydic (or ketonic) form existing. C. F. B.

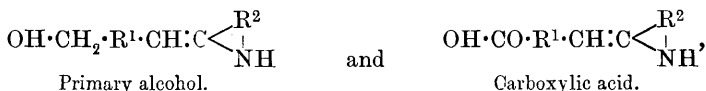
Berberine. JOHANNES GADAMER (*Arch. Pharm.*, 1905, **243**, 31—43).
 —Berberine, $C_{20}H_{19}O_5N$, may exist in three tautomeric forms (compare
 Abstr., 1902, i, 173; preceding abstract) [$R^1 = C_6H_2(OMe)_2$;
 $R^2 = C_6H_2(O_2 \cdot CH_2) \cdot CH_2 \cdot CH_2 \cdot$]:



The free base in the solid state probably has the aldehydic constitution; the ammonium base only exists in aqueous solution, and even then changes in time to the aldehydic form, the alkalinity of the solution gradually disappearing. Its transformation under the influence of alkali into a mixture of dihydroberberine and hydroxyberberine (Abstr., 1902, i, 555) is analogous to that of benzaldehyde into benzyl alcohol and benzoic acid, for the two substances,



may be regarded respectively as the anhydride of the

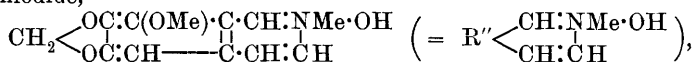


corresponding with the aldehydic form of berberine. Further, an oxime was prepared, although with difficulty; berberine sulphate, mixed with a little water, was treated gradually with sodium hydroxide until it had dissolved as the soluble normal sulphate, excess of the alkali was added, and the precipitated alkaloid was shaken out with ether; to the (filtered) ethereal solution, a hydroxylamine solution was added that had been made by pounding together hydroxylamine hydrochloride and crystallised sodium carbonate, adding some alcohol, then adding a larger volume of ether, and filtering. Flakes first separated which melted at 188—191° and contained C 59·7, H 5·6, N 4·4; then the oxime crystallised out slowly in satisfactory yield; in one experiment, reddish-yellow needles melting and decomposing at 120—122° were obtained in addition. *Berberinaldoxime*, $C_{20}H_{20}O_5N_2$, decomposes at about 165° and is an unstable substance; hydrochloric acid does not form a salt with it, berberine chloride being obtained instead.

As the aldehydic formula contains a :NH group, it might be expected that free berberine (berberinaldehyde) would react with methyl iodide to form a quaternary iodide with the group :NMe₂I; also that it would form a benzoyl derivative with the group :NBz. Neither of these expectations could be realised, however; evidently the aldehydic form of berberine is not a very stable one. C. F. B.

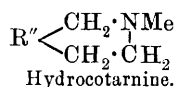
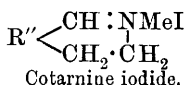
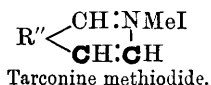
Tarconine Methiodide and its Relations to Cotarnine and Hydrocotarnine. DANIEL BRUNS (*Arch. Pharm.*, 1905, 243, 57—69).—Tarconine methiodide was prepared from narcotine by oxidation with iodine in alcoholic solution, and was reduced to hydrocotarnine with zinc and dilute sulphuric acid. This hydrocotarnine was identical with that obtained by reducing cotarnine, prepared from narcotine by oxidation with dilute nitric acid at 49°, with zinc and dilute sulphuric acid; in both cases, the hydrobromide was obtained anhydrous, contrary to what is often stated. Hydrocotarnine is oxidised by iodine in alcoholic solution at 100° completely to tarconine methiodide; four atoms of hydrogen are lost, just as is the case with tetrahydroberberine and corydaline. Alcoholic iodine in relatively smaller quantity oxidises hydrocotarnine to cotarnine, and cotarnine to tarconine methiodide, but in both cases the yield was far from quantitative. *Tarconine methyl hydrogen sulphate*, $C_{12}H_{11}O_3N \cdot H_2SO_4$, was prepared in the crystalline state and analysed.

Methyltarconium hydroxide, the base corresponding with tarconine methiodide,



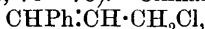
will not condense with hydroxylamine, nor could tarconine methiodide be made to yield definite products by reacting with acetone, chloroform, or ammonium sulphide even in the presence of an alkali. Evidently the base has little tendency to react in a tautomeric aldehydic form, $CHO \cdot R'' \cdot CH:CH \cdot NHMe$ (compare this vol., i, 368).

Since tarconine methiodide is yellow whilst cotarnine iodide and hydrocotarnine are colourless, the chromophoric group must be the $\cdot CH:CH \cdot$ group, the carbon atoms of which are printed in thicker type in the formula of tarconine methiodide below:

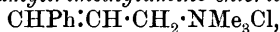


C. F. B.

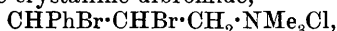
Synthesis of Ephedrine. ERNST SCHMIDT [with F. FLAECHER] (*Arch. Pharm.*, 1905, 243, 73—78).—Cinnamyl chloride,



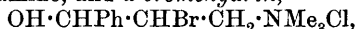
unites with trimethylamine in alcoholic solution at the ordinary temperature to form *cinnamyltrimethylamine chloride*,



which is left as a syrup when the alcohol is evaporated; the *aurichloride* and *platinichloride*, melting at 181° and 209·5—211·5° respectively, were analysed. The chloride in alcoholic solution unites with bromine to form the crystalline dibromide,



which melts at 141—142°. Boiled with water, this yields bromostyrene, trimethylamine, and a *bromohydrin*,



the *platinichloride* of which, less soluble than that of trimethylamine,

was analysed. When the bromohydrin is reduced with zinc and dilute sulphuric acid, there is formed, in addition to an oil much resembling the alcoholic substance, $C_9H_{10}O_3$, obtained by Miller (Abstr., 1903, i, 110) in the distillation of methylephedrine methohydroxide, the chloride of a base, $OH \cdot CHPh \cdot CH_2 \cdot CH_2 \cdot NMe_3Cl$, the *aurichloride* of which melts at 170° . These substances much resemble the isomeric derivatives of ephedrine and ψ -ephedrine, but are devoid of optical activity. When the free base is boiled in aqueous solution, an odour is perceptible resembling that of the oil mentioned above.

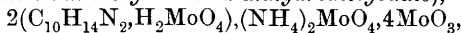
Cinnamylamine, $CHPh \cdot CH \cdot CH_2 \cdot NH_2$, contrary to what has been stated, can be obtained in good yield by allowing cinnamyl chloride to remain for 8 days at the ordinary temperature with ten times its weight of alcoholic ammonia. C. F. B.

Products formed under Various Conditions by the Action of Halogens on *d*-Lupanine. ARTURO SOLDAINI (*Chem. Centr.*, 1905, i, 826; from *Boll. Chim. Farm.*, **44**, 85—90. Compare Abstr., 1902, i, 392, 638).—From the product of the action of bromine on *d*-lupanine, a compound, $C_9H_{15}ON$, has been separated by means of its *platinichloride*, which melts and decomposes at about 200° ; the *platini-chloride* of the base $C_8H_{13}ON$, previously described, melts and decomposes at 201 — 202° . The compound $C_8H_{11}NHBBr$, which is also formed, readily undergoes change on treatment with silver chloride and then with auric chloride, yielding a salt $(C_6H_7N)_2 \cdot HAuCl_4$. The salts $(C_8H_{13}N)_2 \cdot H_2PtCl_6$ and $C_{11}H_{16}O_2N_2 \cdot HBr$ were also prepared, all of which easily undergo change on heating or by the addition of salts.

Lupanine appears to be closely related to sparteine. G. D. L.

Nicotine Camphorate. A. GAWALOWSKI (*Chem. Centr.*, 1905, i, 820; from *Pharm. Post*, **38**, 109).—Nicotine camphorate, formed when nicotine and camphoric acid are heated together at 250° , dissolves in alcohol without subsequently darkening, and dissolves sparingly in water. No turbidity is produced by potassium hydroxide or sulphuric acid in the aqueous solution; light petroleum extracts camphoric or hydroxycamphoric (?) acid from the acid solution. The chief portion of the product, insoluble in water, is yellow and resinous, and dissolves readily in alcohol to a deep yellow solution miscible with water. From the dilute alcoholic solution, light petroleum extracts a yellow constituent; after acidification with sulphuric acid and renewed extraction with light petroleum, traces of a colourless substance are obtained. G. D. L.

Molybdenum Compound of Nicotine. EMIL MESZLÉNYI (*Landw. Versuchs-Stat.*, 1905, **61**, 321—349).—*Nicotine ammonium molybdate* (*dinicotine ammonium molybdo-tetra-anhydromolybdate*),



is prepared by adding to 400 c.c. of a 20 per cent. solution of ammonium molybdate 320 c.c. of 10 per cent. acetic acid and 100 c.c. of a 10 per cent. solution of nicotine. The mixture is shaken several times in a tall cylinder, rapidly filtered, and washed successively with water, alcohol, and ether. It is then dried at 48 — 50° .

It is a white substance, insoluble in water, soluble in acids, and is decomposed by alkalis. When treated with metallic solutions, it yields the corresponding metallic molybdate. It is optically inactive and has a sp. gr. 2.5407. When oxidised in acid and in alkaline solutions, it yields nicotinic acid and dipyridine respectively. It is a strong poison.

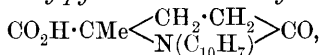
N. H. J. M.

Lactam Formation from γ -Lactones and the Stability of the Pyrrolidone Nucleus. OTTO KÜHLING and FRANZ FALK (*Ber.*, 1905, **38**, 1215—1228).—1-*p*-Tolyl-2-methylpyrrolidone-2-carboxylonitrile is obtained as a yellow oil on condensing ethyl lævulate, hydrogen cyanide, and *p*-toluidine; the corresponding *amide* crystallises in white leaflets melting at 175°. 1-*p*-Tolyl-2-methylpyrrolidone-2-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{CMe}<\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{N}(\text{C}_7\text{H}_7) \end{smallmatrix}>\text{CO}$, prepared by the action of ice-cold fuming hydrochloric acid on the nitrile, crystallises in colourless plates melting at 204°; the *silver* salt separates in crystalline plates, the *methyl* ester was obtained only as a yellow oil, the *anilide* crystallises in plates, the *thioamide* melts and decomposes at 207—208°, and the *amidoxime* forms glistening needles melting at 163.5°.

1-*m*-Tolyl-2-methylpyrrolidone-2-carboxylic acid crystallises in aggregates of needles melting at 136°, the *silver* salt forms plates, and the *methyl* ester rosettes of needles; the *amide* crystallises in thick prisms melting at 198°, the *nitrile* was obtained as a dark brown oil.

1-*o*-Tolyl-2-methylpyrrolidone-2-carboxylic acid crystallises in needles melting at 209.5°; the *amide* separates in column-like crystals which melt at 215.5°, the *nitrile* is a viscid, yellow oil.

1- β -Naphthyl-2-methylpyrrolidone-2-carboxylic acid,



separates in colourless plates melting at 231°, the *zinc* salt crystallises in prisms, the *methyl* ester melts at 104—105°, the *thioamide* at 151°, the *amidoxime* at 176°; the *amide* melts at 223° and the *nitrile*, obtained by condensing ethyl lævulate with hydrogen cyanide and β -naphthylamine, melts at 78.5°.

1- α -Naphthyl-2-methylpyrrolidone-2-carboxylic acid crystallises in needles and melts at 255°, the glistening needles of the *amide* melt at 247.5—248°, the *nitrile* being obtained as a dark brown oil, whilst the *methyl* ester melts at 91°.

1-*m*-Xyl-2-methylpyrrolidone-2-carboxylic acid crystallises in prisms in stellar aggregates melting at 169°, the *copper* salt forms green plates and the *methyl* ester long plates which sinter at 93° and melt at 97.5°. The *amide* crystallises in colourless needles aggregated in rosettes and melts at 196°; the *nitrile* is a light yellow oil.

1-*p*-Xyl-2-methylpyrrolidone-2-carboxylic acid separates from a mixture of acetone and petroleum in glistening needles melting at 226°, the *amide* crystallises and melts at 211°; the *nitrile* is a yellow oil.

1-*as-o*-Xyl-2-methylpyrrolidone-2-carboxylic acid crystallises in needles melting at 192°; the *methyl* ester and *nitrile* are oils, the colourless crystals of the *thioamide* melt at 220°, the *amidoxime* melts at 110°, and the *amide*, which crystallises in plates, melts at 206—207°.

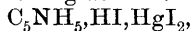
1-vic.-o-Xylyl-2-methylpyrrolidone-2-carboxylic acid forms large needles in stellar aggregates melting at 186° , the thioamide melts at 217° , the amidoxime at 122° , and the amide at 203° . E. F. A.

Synthesis of 2:3:5-Trimethylpyrrole. G. KORSCHUN (*Ber.*, 1905, 38, 1125—1130. Compare Abstr., 1904, i, 615; Feist, Abstr., 1902, i, 488).—Ethyl $\alpha\beta$ -diacetylbutyrate, $\text{CHMeAc}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, is formed by the action of methyl chloroethyl ketone on ethyl sodioacetoacetate in ethereal solution. It reacts with ammonia, slowly at the ordinary temperature, more quickly on warming, to form ethyl 2:3:5-trimethylpyrrole-4-carboxylate, $\text{NH} \begin{array}{c} \text{CMe:CMe} \\ | \\ \text{CMe:C}\cdot\text{CO}_2\text{Et} \end{array}$, which is also formed

when a current of ammonia is passed through a mixture of ethyl acetoacetate and methyl chloroethyl ketone with aqueous ammonia, heated in a reflux apparatus. It crystallises in matted, white needles, melts at $101.5\text{--}102.5^{\circ}$, is only slightly soluble in water or petroleum, but easily so in the other ordinary solvents, is volatile in a current of steam, and gives the pinewood pyrrole reaction. When heated with alcoholic potassium hydroxide at $120\text{--}125^{\circ}$ in a sealed tube for 50 hours, the ethyl ester is hydrolysed, and, the carboxylic acid being unstable at that temperature, the product obtained is 2:3:5-trimethylpyrrole. This is a colourless oil, which boils at $75\text{--}76^{\circ}$ under 14—15 mm., or at 180° under 768 mm. pressure.

Methyl 2:3:5-trimethylpyrrole-4-carboxylate, $\text{C}_9\text{H}_{13}\text{O}_2\text{N}$, is formed when a current of ammonia is passed through a heated mixture of methyl acetoacetate, methyl chloroethyl ketone, and aqueous ammonia; it melts at $124.5\text{--}126^{\circ}$. But if methyl acetoacetate and methyl chloroethyl ketone are shaken with aqueous ammonia, the product obtained forms large crystals, melts at $82\text{--}84^{\circ}$, gives only a slight pinewood reaction, and consists of methyl β -aminocrotonate with traces of the pyrrole derivative. G. Y.

Pyridine Mercuri-iodides. MAURICE FRANÇOIS (*Compt. rend.*, 1905, 140, 861—863).—Complex iodides containing mercury and pyridine are obtained when a solution of pyridine hydriodide acts on mercuric iodide, or when a solution of pyridine hydrochloride is added to an aqueous solution containing 100 grams of mercuric iodide and 75 grams of potassium iodide per litre. The compound $(\text{C}_5\text{NH}_5\text{HI})_2\cdot\text{HgI}_2$ is formed when pyridine is dissolved in concentrated hydrochloric acid and the solution mixed with five times its volume of the mercuric iodide solution. It forms colourless plates melting at 159° . The compound



formed in similar circumstances when the proportion of pyridine is smaller, crystallises in pale yellow needles which melt at 151° . When a solution of pyridine hydriodide is warmed with a large excess of mercuric iodide, two other iodides are obtained, $(\text{C}_5\text{NH}_5\text{HI})_2\cdot 3\text{HgI}_2$, which forms yellow crystals melting at 101° , and $\text{C}_5\text{NH}_5\text{HI}\cdot 2\text{HgI}_2$, which crystallises in golden-yellow plates melting at 121° . These complex iodides are all decomposed by water with precipitation of mercuric iodide. H. M. D.

Action of Formaldehyde on Pyridine. EMANUEL FORMÁNEK (*Ber.*, 1905, 38, 944—945).—A condensation product, C_5H_5N, H_2CO , is formed when pyridine is heated for several hours on the water-bath with an excess of 40 per cent. formaldehyde. It crystallises from hot alcohol in rosettes of small needles, is readily decomposed into its components, and yields a *platinichloride* which is also readily decomposed. J. J. S.

Ammonium Compounds. XVIII. Formation and Decomposition of Quaternary Ammonium Compounds of the Inert Bases. HERMAN DECKER [with S. GADOMSKA, F. SANDBERG, and A. STAVROLOPOULOS] (*Ber.*, 1905, 38, 1144—1155).—Many "inert" bases, such as the 8-nitroquinolines, which do not combine additively with methyl iodide, readily interact with methyl sulphate; from the additive compound formed, the methiodide of the base may be obtained by the action of potassium iodide. Such methiodides are on warming rapidly decomposed quantitatively into methyl iodide and the base; they may be analysed by absorbing the methyl iodide with alcoholic silver nitrate. Methyl sulphate may in many instances profitably replace methyl iodide as a methylating agent, owing to its entering into action at 100° ; the substances may be heated together in an open vessel, but moisture should be excluded as much as possible.

8-Nitro-1-methylquinolinium 1-methosulphate, forms white, deliquescent crystals, is very soluble in water, and with sodium picrate gives the *picrate*, $C_{16}H_{11}O_9N_5$, crystallising in yellow needles and melting at 176° ; with sodium dichromate, it gives an analogous *dichromate* and with potassium iodide 8-nitroquinoline methiodide is obtained. This crystallises in blue cubes and decomposes when slowly heated at about 120° .

8-Nitroquinoline ethiodide forms orange-red crystals. On oxidising 8-nitro-1-methylquinolinium 1-ethosulphate with an alkaline solution of potassium ferrieyanide, 8-nitro-1-ethyl-2-quinolone is obtained, which crystallises from methyl alcohol in sheaf-like aggregates and melts at 96° . The substance previously described (Decker and Stavropolopoulos, *Abstr.*, 1903, i, 719) as 8-nitro-1-ethyl-2-quinolone, melting at 87° and obtained by the action of ethyl iodide on the sodium derivative of nitrocarbostyryl, is really the *ethyl ether*, $NO_2 \cdot C_9NH_5 \cdot OEt$, of 8-nitrocarbostyryl. Similarly, the 8-nitro-1-methyl-2-quinolone (*Abstr.*, 1901, i, 654) melting at 125° is 8-nitrocarbostyryl methyl ether.

6:8-Dinitroquinoline methiodide crystallises in needles, decomposes at 172° , and on careful oxidation gives 6:8-dinitro-1-methyl-2-quinolone melting at 185° .

3-Bromo-8-nitroquinoline methiodide decomposes at about 145° ; 3-bromo-8-nitro-1-methyl-2-quinolone crystallises from alcohol in yellow needles and melts at 185 — 186° .

6:8-Dibromoquinoline methiodide decomposes at 178° ; 6:8-dibromo-1-methyl-2-quinolone crystallises from methyl alcohol in white needles, melts at 125° , and is converted by phosphorus pentabromide into 2:6:8-tribromoquinoline, which crystallises in needles and melts at 165° . When the latter is heated with hydrochloric acid, 6:8-dibromocarbostyryl, melting at 230° , is obtained.

5-Nitro-1:8-dimethyl-2-quinolone, prepared from 5-nitro-8-methylquinoline, crystallises in yellow needles and melts at 139°.

5:8-Dibromoquinoline methiodide crystallises in red needles and decomposes at 166°.

By means of methyl sulphate, 5-nitroquinoline can readily be separated from 8-nitroquinoline; at 80° only the 5-nitroquinoline gives rise to a quaternary salt, the 8-isomeride remaining unaffected.

Phenylacridine methiodide begins to decompose at 220—222°. Phenylacridine ethiodide decomposes at 215°. W. A. D.

6-Hydroxyquinolones and some Alkyl Haloid Derivatives of 5-Bromo-6-hydroxyquinoline. JOH. HOWITZ and M. BÄRLOCHER (*Ber.*, 1905, 38, 887—892. Compare *Abstr.*, 1903, i, 279).—5-Chloro-

6-hydroxy-1-ethylquinolone, $\text{CH:CH}\cdot\text{C}\cdot\text{NEt}\cdot\text{CO}$
 $\text{OH}\cdot\text{C}\equiv\text{CCl}\cdot\text{C}\cdot\text{CH:CH}$, formed when 5-bromo-6-ethoxy-1-ethylquinolone is heated with concentrated hydrochloric acid in a sealed tube at 160—170°, crystallises in slender, white needles or prisms and melts at 210—212°. Similarly, 5-chloro-6-hydroxyquinoline is formed when 5-bromo-6-ethoxyquinoline is heated with concentrated hydrochloric acid.

5-Bromo-6-hydroxy-1-methylquinolone is formed by heating the corresponding methoxy-compound with hydrobromic acid at 130—140°; it crystallises in slender, yellow needles or prisms, melts at 271°, and forms an insoluble, crystalline sodium derivative.

5-Bromo-6-hydroxyquinoline methiodide, formed by heating the quinoline with methyl iodide at 90—100°, crystallises in yellow needles and melts and decomposes at 156—158°. The methochloride, $\text{C}_{10}\text{H}_9\text{ONClBr}\cdot 2\text{H}_2\text{O}$, formed by treating the methiodide with silver chloride, crystallises in slender, yellow needles and melts at 212—215°; the platinichloride, $(\text{C}_{10}\text{H}_9\text{ONClBr})_2\cdot\text{PtCl}_4\cdot 3\text{H}_2\text{O}$, crystallises in glistening, red prisms and melts at 270°; the ammonium base, $\text{C}_9\text{H}_6\text{BrO}\cdot\text{NMe}\cdot\text{OH}$, formed by the action of potassium hydroxide or moist silver oxide on the methochloride, separates from water in slender, glistening, red crystals and melts and decomposes at 218°. The ethobromide, $\text{C}_{11}\text{H}_{11}\text{ONBr}_2$, crystallises in colourless, glistening, short prisms, melts at 235°, and when treated with potassium hydroxide or moist silver oxide yields the base



which crystallises in glistening, red prisms and melts and decomposes at 204—206°. The benzylochloride of 5-bromo-6-hydroxyquinoline, $\text{C}_{16}\text{H}_{13}\text{ONClBr}\cdot\text{H}_2\text{O}$, crystallises in small, yellow prisms and melts at 100—105°, or, when anhydrous, at 139—140°; the platinichloride, $(\text{C}_{16}\text{H}_{13}\text{ONClBr})_2\cdot\text{PtCl}_4\cdot 3\text{H}_2\text{O}$, crystallises in slender, red prisms and melts at 198°; the base, $\text{OH}\cdot\text{C}_9\text{H}_5\text{BrO}\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{OH}\cdot\text{H}_2\text{O}$, crystallises in slender, carmine needles or leaflets and melts and decomposes at 112°.

G. Y.

Action of Phenylhydrazine on Alkyl Bromides and Iodides. JULES ALLAIN-LE CANU (*Bull. Soc. chim.*, 1905, [iii], 33, 327—335. Compare *Abstr.*, 1903, i, 778).—Phenyldipropylhydrazine bromide,

$N_2H_2Pr^a_2PhI$, obtained by the general method (*loc. cit.*), forms faintly yellow, triclinic crystals [$a:b:c=0.7029:1:0.5594$; $\alpha=89^\circ17'$, $\beta=86^\circ37'$, $\gamma=93^\circ48'$], melts at 85° , and is readily soluble in alcohol, somewhat less so in water. *Phenyldibutylhydrazine bromide* forms slightly yellow, triclinic crystals [$a:b:c=0.7731:1:0.5273$; $\alpha=89^\circ56'$, $\beta=89^\circ58'$, $\gamma=98^\circ29'$], melts at 148° , and is fairly soluble in alcohol, less so in water. *Phenyldibutylhydrazine iodide*, $N_2H_2(C_4H_9)_2PhI$, forms colourless, triclinic crystals [$a:b:c=2.3244:1:1.191$; $\alpha=91^\circ0'$, $\beta=87^\circ37'$, $\gamma=101^\circ43'$], melts at 95° , is moderately soluble in alcohol, and less so in water. *Phenyldimethylhydrazine iodide*, $N_2H_2Me_2\cdot PhI$ (Genvresse and Bourcet, *Abstr.*, 1899, i, 502), forms monoclinic crystals [$a:b:c=1.8917:1:1.3967$; $\beta=91^\circ10'$]. The crystallographic measurements recorded were made by de Schulten.

The iodides of phenylisopropylhydrazine and phenyldiisobutylhydrazine and the bromide of phenyldiisomethylhydrazine could not be prepared by the general method. T. A. H.

Conversion of Schiff's Bases into Hydrazones, Semicarbazones, and Oximes. HANS OTT (*Monatsh.*, 1905, 26, 335—348. Compare Ofner, *Abstr.*, 1904, i, 818; Ullmann and Frey, *Abstr.*, i, 423).—With phenylhydrazine, *p*-bromophenylhydrazine, *as*-phenylmethylhydrazine, *as*-phenylethylhydrazine, *as*-diphenylhydrazine, *as*-benzoylphenylhydrazine, semicarbazide, or hydroxylamine in alcoholic solution, the following Schiff's bases are converted into the corresponding hydrazones, semicarbazones, or oximes: benzylideneaniline, *m*-nitrobenzylideneaniline, *p*-methoxybenzylideneaniline, *p*-hydroxy-*m*-methoxybenzylideneaniline, piperonylideneaniline, anilino-opianic acid, benzophenoneanilide, benzylidene-*m*-nitraniline, benzylidene-*o*-toluidine, benzylidene-*m*-xylidine, benzylidene- β -naphthylamine. Anilpyruvic acid does not enter into the reaction. *as*-Diphenylhydrazine, semicarbazide, and hydroxylamine are used in the form of their hydrochlorides in presence of sodium acetate.

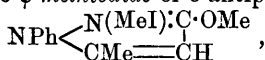
The following new substances are described: *m*-nitrobenzylidene-*p*-bromophenylhydrazone crystallises in red needles and melts at 150 — 152° . *p*-Methoxybenzylideneaniline melts at 60 — 62° . *p*-Methoxybenzylidene-*p*-bromophenylhydrazone crystallises in brown leaflets and melts at 146 — 147° . *p*-Methoxybenzylidene-*as*-phenylmethylhydrazone crystallises in white needles and melts at 110 — 112° . *p*-Hydroxy-*m*-methoxybenzylideneaniline crystallises in yellow needles and melts at 152 — 153° . *p*-Hydroxy-*m*-methoxybenzylidenephénylmethylhydrazone crystallises in white needles and melts at 116° . *p*-Hydroxy-*m*-methoxybenzylidenephénylethylhydrazone forms yellow crystals and melts at 83 — 86° . *p*-Hydroxy-*m*-methoxybenzylidenediphenylhydrazone crystallises in hexagonal leaflets and melts at 125 — 127° . *p*-Hydroxy-*m*-methoxybenzylidenephénylbenzylhydrazone forms white crystals and melts at 172 — 173° . *p*-Hydroxy-*m*-methoxybenzylidenebenzoylphenylhydrazone crystallises in white needles and melts at 171 — 173° . *p*-Hydroxy-*m*-methoxybenzylidenesemicarbazone melts at 229° . *Piperonylidenephenylbenzylhydrazone* forms white needles and melts at 127 — 130° . *Piperonylidenesemicarbazone* crystallises in white leaflets and melts at 230 — 233° . G. Y.

Mutual Replacement of Sugar Residues in Hydrazones. EMIL VOTOČEK and RUDOLF VONDRÁČEK (*Ber.*, 1905, **38**, 1093—1095. Compare Abstr., 1904, i, 1055).—In aqueous or aqueous alcoholic solution, galactosephenylhydrazone and mannose form mannosephenylhydrazone and galactose; similarly, dextrosephenylmethylhydrazone and galactose form galactosephenylmethylhydrazone and dextrose. Dextrosediphenylhydrazone and arabinose react, when warmed with acetic acid in aqueous-alcoholic solution, to form arabinosediphenylhydrazone and dextrose. In aqueous solution, galactosephenylhydrazone and dextrosephenylmethylhydrazone form galactosephenylmethylhydrazone and dextrosephenylhydrazone. Those reactions which take place in neutral solution are accelerated by addition of acetic acid; in each case, a less soluble hydrazone is formed. G. Y.

3-Pyrazolones. AUGUST MICHAELIS (*Annalen*, 1905, **338**, 267—321. Compare Abstr., 1903, i, 288; 1904, i, 124, 624; and *Ber.*, 1909, **38**, 154).—1-Phenyl-5-methyl-3-pyrazolone, $\text{NPh} \begin{smallmatrix} \text{NH-CO} \\ \text{CMe:CH} \end{smallmatrix}$, which hitherto has only been prepared with difficulty, can now be readily obtained by the action of phosphorus pentachloride on a mixture of acylphenylhydrazine and ethyl acetoacetate. It has both acid and basic properties, and with phosphorus oxychloride yields 3-chloro-1-phenyl-5-methylpyrazole, $\text{NPh} \begin{smallmatrix} \text{N=CCl} \\ \text{CMe:CH} \end{smallmatrix}$, and with acid chlorides, benzoyl chloride, and benzenesulphonic chloride, derivatives which are either amides, $\text{NPh} \begin{smallmatrix} \text{NBz:CO} \\ \text{CMe:CH} \end{smallmatrix}$, or esters, $\text{NPh} \begin{smallmatrix} \text{N=C:OBz} \\ \text{CMe:CH} \end{smallmatrix}$. A methyl ether is formed by the action of methyl iodide and alkali hydroxide. Benzaldehyde (1 mol.) condenses with two mols. of the pyrazolone. The hydrogen atom in position 4 is readily replaced by halogens, and sodium nitrite and acetic acid convert the pyrazolones into green nitroso-derivatives. When heated with methyl iodide, a methiodide, 3-antipyrine, is obtained. Benzenediazonium chloride reacts with 3-pyrazolone, giving 4-azobenzene derivatives (see this vol., i, 392). 3-Pyrazolone differs from 5-pyrazolone in not giving the pyrazole-blue reaction.

[With CARL MEYER.]—1-Phenyl-5-methyl-3-pyrazolone is prepared by adding phosphorus pentachloride slowly to a mixture of acetylphenylhydrazine and ethyl acetoacetate and finally heating to 100°; the mixture is then poured into water, ammonia added, and lastly the solution made exactly neutral with hydrochloric acid; it crystallises in needles melting at 166° and boiling at 344—345° (corr.), and exists also in a labile form melting at 157°. The *hydrochloride* crystallises (with 2H₂O) in needles melting at 129°; the *sulphate*, which also crystallises in needles, is anhydrous and melts at 84°. The *picrate* crystallises in yellow plates melting at 141°. The *benzoyl* derivative, prepared by shaking an alkaline solution of the pyrazolone with benzoyl chloride, crystallises in needles melting at 64—65°, and the corresponding *benzenesulphonate* in needles melting at 76°. 4-Chloro-1-phenyl-5-methyl-

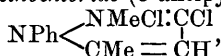
3-pyrazolone, $\text{NPh} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CMe} \cdot \text{CCl} \end{smallmatrix}$, prepared by passing chlorine into a chloroform solution of the pyrazolone or by heating the pyrazolone with phosphorus pentachloride at 150° , forms prisms melting at 261° ; the corresponding bromo-derivative forms leaflets melting and decomposing at 241° . The benzylidene derivative, $\text{CHPh} \left[\text{OC} \begin{smallmatrix} \text{CMe} \cdot \text{NPh} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \right]_2$, prepared by heating the pyrazolone with benzaldehyde at 100° , is a white powder melting at 270° ; the compound with anisaldehyde melts at 287° . 3-Methoxy-1-phenyl-5-methylpyrazole (ψ -3-antipyrene), $\text{NPh} \begin{smallmatrix} \text{N} = \text{C} \cdot \text{OMe} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix}$, is formed together with 3-antipyrene when a mixture of sodium ethoxide and the pyrazolone are treated with methyl iodide, and is a colourless oil boiling at $150\text{--}160^\circ$ under 16 mm. and at $273\text{--}275^\circ$ under the ordinary pressure. When heated with methyl iodide, the ψ -methiodide of 3-antipyrene,



is formed as colourless needles melting at 198° . The 3-antipyrene (1-phenyl-2 : 5-dimethyl-2 : 3-oxypyrazole), $\text{CMe} \begin{smallmatrix} \text{CH} - \text{C} \\ \text{NPh} \cdot \text{NMe} \end{smallmatrix} \text{O}$, is identical with Lederer's isoantipyrene (*J. pr. Chem.*, 1892, [ii], 45, 40).

3-Chloro-1-phenyl-5-methylpyrazole, prepared by heating the pyrazolone with phosphorus oxychloride at 210° , is a viscid, colourless liquid, not solidifying at -10° , and boiling at 170° under 15 mm. and at 304° under the ordinary pressure, and having a sp. gr. 1.2054 at 19° and n_D 1.5845. The 3 : 5-dichloro-compound, $\text{NPh} \begin{smallmatrix} \text{N} = \text{CCl} \\ \text{CMe} \cdot \text{CCl} \end{smallmatrix}$, prepared by heating the pyrazolone at 200° with phosphorus pentachloride, is a liquid. 3-Chloro-4-bromo-1-phenyl-5-methylpyrazole, prepared from 3-chloro-compound, is a yellowish-green oil boiling at 194° under 15 mm. pressure.

The methiodide of 3-chloro-1-phenyl-5-methylpyrazole crystallises in needles decomposing at 177° ; the methobromide crystallises in needles melting at 197° . The methochloride (3-antipyrene chloride),



prepared from the methiodide and silver chloride or from 3-antipyrene and phosphorus oxychloride, crystallises in needles with H_2O melting and decomposing at 100° ; its aqueous solution has a bitter taste and gives precipitates with potassium ferro- and ferri-cyanides, with phosphotungstic acid, bromine water, hydrogen platinichloride, hydrogen aurichloride, and picric acid. The platinichloride crystallises in red leaflets melting at 218° .

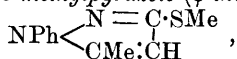
[With WILHELM HAHN.]—2 : 3-Thio-1-phenyl-2 : 5-dimethylpyrazole (3-thiopyrene), $\text{CMe} \begin{smallmatrix} \text{CH} - \text{C} \\ \text{NPh} \cdot \text{NMe} \end{smallmatrix} \text{S}$, is obtained when potassium hydrosulphide and the methiodide of 3-chloro-1-phenyl-5-methylpyrazole are

mixed in concentrated solution, and forms colourless crystals melting at 136° ; when distilled, it passes into a ψ -compound; its aqueous solution gives precipitates with bromine water, mercuric chloride, potassium ferro- and ferri-cyanides, hydrogen platinichloride and aurichloride, picric and sulphurous acids. The *hydriodide* crystallises in needles melting at 176° . The *methiodide* forms white crystals melting at 168° , the *methochloride* hygroscopic prisms melting at 184° , the *platinichloride* yellowish-red needles melting and decomposing at 205° , the *ethiodide* needles melting at 121° , the *isopropiodide* (with $2\text{H}_2\text{O}$) crystals melting at 99° , the *benzyl-iodide* needles melting at 146° , the *benzoyl-chloride* unstable crystals melting at 83° , and the *benzoyl-iodide* needles melting at 163° .

2 : 3-*Trioxythio-1-phenyl-2 : 5-dimethylpyrazole* (3-*thiopyrinetrioxyde*),

$$\text{CMe} \begin{array}{c} \text{CH} - \text{C} - \text{SO}_2 \\ \diagdown \quad \diagup \\ \text{NPh} \cdot \text{NMe} \cdot \text{O} \end{array}$$
, prepared by passing chlorine into an aqueous solution of 3-thiopyrine, or by treating with sodium sulphite the methiodide of 3-chloro-1-phenyl-5-methylpyrazole, crystallises in prisms melting at 285° .

3-*Thiomethyl-1-phenyl-5-methylpyrazole* (ψ -*thiopyrine*),

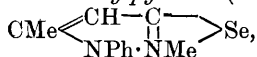


prepared by dry distillation of thiopyrine or its methiodide under reduced pressure, forms a colourless liquid boiling at 175° under 10 mm., at 194° under 22 mm., and at 357° under the ordinary pressure. Its *hydrochloride* crystallises in needles melting at 132° , its *platinichloride* with $2\text{H}_2\text{O}$ in yellow needles melting and decomposing at 130° ; the *methiodide* is identical with that from 3-thiopyrine, and the *ethiodide* forms prisms melting at 148° .

3-*Methylsulphone-1-phenyl-5-methylpyrazole*, $\text{NPh} \begin{array}{c} \text{N} = \text{C} \cdot \text{SO}_2\text{Me} \\ \diagdown \quad \diagup \\ \text{CMe} : \text{CH} \end{array}$,

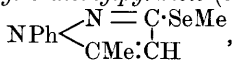
prepared by oxidation of ψ -thiopyrine with permanganate, crystallises in needles melting at 105° . 4-*Bromo-3-thiomethyl-1-phenyl-5-methylpyrazole* (*bromo-3- ψ -thiopyrine*), prepared from bromine and ψ -thiopyrine in chloroform solution, crystallises in colourless needles melting at 107° .

2 : 3-*Seleno-1-phenyl-2 : 5-dimethylpyrazole* (3-*selenopyrine*),



is prepared from potassium hydroselenide and 3-antipyryne chloride or the methiodide of 1-phenyl-5-methyl-3-pyrazolone, crystallises in yellow leaflets melting at 168° , and gives precipitates with the same reagents as the analogous sulphur compound. The *platinichloride* is a reddish-brown powder. The crystalline *mercurichloride* melts at 198° . The *hydriodide* forms unstable, yellow needles melting at 183° , the *methiodide* prisms melting at 80° , and the *ethiodide* needles melting at 132° . The *selenopyrine* forms, with bromine, a *tetrabromide* as red crystals melting at 69° , becoming a *dibromide* on heating; the latter crystallises in golden-yellow needles melting at 174° , and when heated with aqueous sodium carbonate yields the *methobromide* of 1-phenyl-5-methylpyrazole.

3-Selenomethyl-1-phenyl-5-methylpyrazole (3- ψ -selenopyrine),



prepared by distilling the methiodide of 3-selenopyrine under reduced pressure, is a colourless liquid of unpleasant smell, boiling at 195° under 13 mm. pressure; its *hydrochloride* is a crystalline solid melting at 135° , and its *platinichloride*, crystallising with $2\text{H}_2\text{O}$, sinters at high temperatures; the *methiodide* is identical with that of 3-selenopyrine, and the *ethiodide* crystallises in needles melting at 110° . 3- ψ -Selenopyrine *tetrabromide*, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{Br}_4\text{Se}$, is a yellowish-brown powder melting at 191° , and is converted by heating into the *bromide* of 3- ψ -selenopyrine, $\text{C}_{11}\text{H}_{11}\text{N}_2\text{BrSe}$, crystallising in white needles melting at 178° .

[With JOHANN BEHRENS.]—The *tolylmethylpyrazolones* are prepared from acetyltolylhydrazines and ethyl acetoacetate. 1-p-Tolyl-5-methyl-3-pyrazolone, $\text{C}_7\text{H}_7 \cdot \text{N} \begin{array}{c} \text{NH} - \text{CO} \\ \text{CMe} : \text{CH} \end{array}$, crystallises in needles melting at 196° ,

and the *ortho-derivative* in prisms melting at 169° . The *hydrochloride* of the *para-compound* crystallises in plates melting at 206° , and that of the *ortho-compound* in prisms melting at 190° ; the *nitrates* were both prepared. The *benzoyl* derivative of the *para-compound* crystallises in needles melting at 47° , and that of the *ortho-compound* in prisms melting at 72° . The benzenesulphonic derivative of the *para-compound* crystallises in needles melting at 55° , and that of the *ortho-compound* at 80° . The *benzylidene* derivative of the *para-compound* is a crystalline powder melting at 278° ; the derivatives of anisaldehyde are powders, the *para-derivative* melting at 270° , and the *ortho-* at 295° . 3-Chloro-1-tolyl-5-methylpyrazoles are prepared from the pyrazolone and phosphorus oxychloride; the *para-compound* is crystalline and melts at 49° , and boils at 176° under 15 mm. pressure, whilst the *ortho-compound* is an oil boiling at 162° under 15 mm. pressure. The *methiodide* of the *para-tolylchloropyrazolone* forms crystals melting at 202° , and that of the *ortho-derivative* crystals melting at 179° . 3-p-Tolylpyrine, $\text{CMe} \begin{array}{c} \text{CH} - \text{C} - \\ \text{N}(\text{C}_7\text{H}_7) \cdot \text{NMe} \end{array} > \text{O}$,

crystallises in prisms melting at 98 – 100° and gives in aqueous solution with ferric chloride a dark red coloration; the *ortho-derivative* crystallises in needles melting at 97° ; the *hydrochlorides* crystallise with H_2O , the *para-compound* melting at 133° and the *ortho-* at 186° . The *picrate* of the *p-tolyl* compound crystallises in yellow leaflets melting at 181° , and of the *o-tolyl* compound in yellow needles melting at 165° .

3-p-Tolylthiopyrine crystallises in leaflets melting at 223° , the *ortho-compound* in leaflets melting at 133° ; they both yield yellow, crystalline precipitates with sulphur dioxide, that from the *ortho-derivative* alone being stable, and melting at 112° . The *methiodide* forms crystals melting at 168° , and that of the *ortho-compound* at 173° . *Thiotolylpyrinetrixoxides*, $\text{C}_{12}\text{H}_{14}\text{O}_3\text{N}_2\text{S}$, are prepared from the methiodide and sodium sulphite, the *para-compound* melting at 281° and the *ortho-compound* at 278° . 3- ψ -Thiotolylpyrines (3-thiomethyl-1-tolyl-5-methylpyrazoles), $\text{C}_{12}\text{H}_{14}\text{N}_2\text{S}$, are prepared by distilling the methiodide under reduced pressure, the *para-compound* is an oil boiling at 151° under 31 mm., and the *ortho-com*.

pound an oil boiling at 135° under 32 mm. pressure. When oxidised with permanganate, they yield the *sulphones*; both crystallise in needles, the *para-compound* melting at 85° and the *ortho-compound* at 122°.

K. J. P. O.

4-Nitro-5-pyrazolone. HENRY B. HILL and OTIS F. BLACK (*Amer. Chem. J.*, 1905, 33, 292—300).—It has been shown by Hill and Hale (*Abstr.*, 1903, i, 401) that by the action of sodium hydroxide on nitromalonic diacetyldialdoxime a substance is produced which is isomeric with fulminuric acid. It is now found that it is

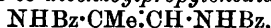
4-nitro-5-pyrazolone, $\text{NO}_2 \cdot \text{CH} \cdot \text{CO} \begin{matrix} \text{CH}=\text{N} \\ \text{NH} \end{matrix}$; it forms small, colourless crystals, melts at 136—137°, and is soluble in water, alcohol, or ether, but less so in benzene, chloroform, or light petroleum; its *sodium*, *silver*, *barium*, and *lead* derivatives are described. On heating 4-nitro-5-pyrazolone with excess of phosphorus oxychloride in a sealed tube at 100°, 5-chloro-4-nitropyrazole (Meder, *Inaug. Diss.*, 1901) is obtained, which crystallises in white, slender needles, melts at 186—187°, and is freely soluble in alcohol, acetone, or hot water, and slightly so in ether, chloroform, or cold water.

By the action of bromine on the sodium derivative of 4-nitro-5-pyrazolone, *tribromopyrazole*, $\text{NH} \begin{matrix} \text{N}=\text{CBr} \\ \text{CBr}:\text{CBr} \end{matrix}$, is produced, which forms white, silky needles, sublimes at about 120°, melts at 181°, is volatile with steam, and is soluble in alcohol or ether; its *acetyl* derivative crystallises in white needles and melts at 105—106°; the *silver* derivative is also described.

When tribromopyrazole is prepared by the action of bromine vapour on sodium 4-nitro-5-pyrazolone, a small quantity of another *substance* is simultaneously produced, which crystallises in white needles, melts at 163—164°, yields an acetyl derivative, and is probably dibromonitropyrazole; it combines with bromine to produce an additive compound which forms orange-coloured crystals, and is insoluble in cold water, but is decomposed by boiling water with evolution of bromine and formation of the white compound melting at 163—164°.

E. G.

Transformation of Dextrose into Methylininazole. ADOLF WINDAUS and FRANZ KNOOP (*Ber.*, 1905, 38, 1166—1170).—On leaving dextrose at the ordinary temperature with zinc hydroxide dissolved in ammonia, it gives rise to 10 per cent. of its weight of pure 4-(or 5)-methylininazole [4-(or 5)-methylglyoxaline], $\text{CMe} \cdot \text{NH} \begin{matrix} \text{CH} \\ \text{CH}=\text{N} \end{matrix} \text{CH}$, identical with Gabriel and Pinkus' base (*Abstr.*, 1893, i, 734; compare Jowett and Potter, *Trans.*, 1903, 83, 464). This substance, when subjected to the Schotten-Baumann method of benzoylation, gives rise to *dibenzoylpropylenediamine*,



which crystallises from alcohol in long needles and melts at 142°. 4-(or 5)-*Methylglyoxaline oxalate* crystallises from acetone and melts

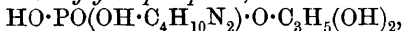
and decomposes at 205—206°; the corresponding *picrate* crystallises from water and melts at 159—160°; the *platinichloride* crystallises in needles and melts at 206°. The above-described method gives an easy means of preparing 4-(or 5-)methylglyoxaline.

The production of methylglyoxaline from dextrose throws light on the origin of naturally occurring glyoxaline derivatives and on the transformation of dextrose into lactic acid. It is probable that the latter takes place through the primary formation of glyceric aldehyde and the subsequent transformation of this into methylglyoxal and lactic acid; that methylglyoxal is capable of being formed directly from dextrose is shown by the formation of methylglyoxaline, which probably occurs according to the equation $\text{CH}_3\cdot\text{CO}\cdot\text{CHO} + 2\text{NH}_3 + \text{CH}_2\text{O} \rightarrow \text{CMe}\cdot\text{NH} \begin{smallmatrix} \text{H} \\ | \\ \text{CH}-\text{N} \end{smallmatrix} \gg \text{CH}$; the formaldehyde necessary may be either directly produced from the dextrose or by the decomposition of methylglyoxal, acetic acid being then also formed.

Among the other products of the action of ammoniacal zinc hydroxide on dextrose is the lactone saccharin, $\text{C}_6\text{H}_{10}\text{O}_5$. W. A. D.

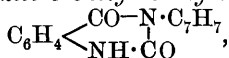
Piperazine Glycerophosphates. A. ASTRUC (*Compt. rend.*, 1905, 140, 727—730).—*Piperazine dihydrogen bisglycerophosphate*, $[\text{PO}(\text{OH})_2\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2]_2\cdot\text{C}_4\text{H}_{10}\text{N}_2\cdot\text{H}_2\text{O}$, obtained as a transparent non-crystalline mass by evaporating an aqueous solution of glycerophosphoric acid (2 mols.) and piperazine (1 mol.), is neutral towards methyl-orange and acid towards phenolphthalein, and requires 3 mols. of an alkali to neutralise it in the presence of the latter indicator according to the equation $[\text{PO}(\text{OH})_2\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2]_2\cdot\text{C}_4\text{H}_{10}\text{N}_2 + 3\text{MOH} = \text{PO}(\text{OM})_2\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2 + \text{MO}\cdot\text{PO}(\text{OH}\cdot\text{C}_4\text{H}_{10}\text{N}_2)\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{OH})_2 + 3\text{H}_2\text{O}$.

Hydrogen piperazine glycerophosphate,



obtained by mixing equivalent quantities of piperazine and glycerophosphoric acid in aqueous or alcoholic solution, crystallises in brilliant plates, melting and decomposing at 155°, readily soluble in water, and insoluble in absolute alcohol. It is alkaline towards methyl-orange and acid towards phenolphthalein, requiring 1 mol. of acid to render it neutral towards the former or 1 mol. of alkali to render it neutral towards the latter indicator. M. A. W.

Derivatives of 2:4-Diketotetrahydroquinazoline. FRANZ KUNCKELL (*Ber.*, 1905, 38, 1212—1215).—2:4-Diketo-3-bromophenyl-tetrahydroquinazoline crystallises in colourless plates melting between 295° and 298°. 2:4-Diketo-3-o-tolyltetrahydroquinazoline,



prepared by heating together anthranilic acid and o-tolylcarbamide at 165°, crystallises from alcohol in colourless, glistening plates melting at 243—244°; 2:4-diketo-3-p-tolyltetrahydroquinazoline forms colourless plates, which melt at 259—260°. By the interaction of anthranilic acid and guanidine carbonate, a colourless substance, $\text{C}_8\text{H}_7\text{ON}_3$, probably the 2-imino-4-ketotetrahydroquinazoline mentioned

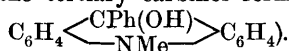
by Griess (Abstr., 1880, 803), is obtained; this melts above 280° and can be sublimed. E. F. A.

Acetylation of Dihydrophenazine. MICHAEL M. TICHWINSKY and L. WOŁOCHOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 8—11).—On acetylating dihydrophenazine, it yields *acetyldihydrophenazine*, $C_6H_5 \begin{smallmatrix} \swarrow NAc \\ \searrow N \end{smallmatrix} C_6H_4$, which crystallises from alcohol or benzene in slender, colourless rhombohedra melting at 255° and difficultly soluble in all solvents. This same compound is obtained when phenazine is reduced in alcoholic ammonia solution and the product so obtained acetylated. Hence dihydrophenazine and, consequently, also phenazine must possess unsymmetrical formulæ. T. H. P.

***m*-Tolylsemicarbazide.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 157572).—*m*-Tolylhydrazine hydrochloride reacts with potassium cyanate in cold aqueous solution to form *m*-tolylsemicarbazide: $C_6H_4Me \cdot NH \cdot NH_2 \cdot HCl + KCNO = C_6H_4Me \cdot NH \cdot NH \cdot CO \cdot NH_2 + KCl$. *m*-Tolylsemicarbazide crystallises from hot water or dilute alcohol in white, glistening leaflets, melts at 183 — 184° , and dissolves sparingly in cold water or ether. Its solution reduces silver nitrate. Unlike the corresponding phenyl, *p*-tolyl and *o*-tolyl derivatives, it is tasteless and non-irritant.

In place of metallic cyanates, carbamide or ethyl carbamate may be employed in the preparation. C. H. D.

Condensation of ψ -Ammonium Bases with Hydroxylamine and *as*-Dimethyl-*p*-phenylenediamine. JOHANNES GADAMER (*Arch. Pharm.*, 1905, 243, 43—49).—Experiments of a preliminary character have shown that the base of "crystal violet" does not condense with *p*-dimethylaminoaniline in ethereal solution, whereas those of quinoline methiodide and acridine methiodide appear to yield condensation products, and that of phenylacridine methiodide yields a product $C_{28}H_{27}N_3$ (probably $NMe_2 \cdot C_6H_4 \cdot N : CPh \cdot C_6H_4 \cdot NMe \cdot C_6H_5$, derived from the ketonic form, $CPhO \cdot C_6H_4 \cdot NMe \cdot C_6H_5$, of phenylmethylacridinium hydroxide, $C_6H_4 \begin{smallmatrix} \swarrow CPh \\ \searrow NMe(OH) \end{smallmatrix} C_6H_4$), which melts at 188 — 189° . Phenylmethylacridinium hydroxide also forms with hydroxylamine in ethereal solution an *oxime* which has no sharp melting point; this is accompanied by a substance that is more soluble in ether, melts at 131° , and contains N 7.7 per cent. (possibly bisphenylmethylacridine hydroxylamine, derived from the tertiary carbinol form,



It would appear, therefore, that just those ψ -ammonium bases which, by the opening of a ring, can change into aldehydic or ketonic forms, do condense with α -dimethyl-*p*-phenylenediamine or hydroxylamine to form more or less stable products (compare this vol., i, 368).

C. F. B.

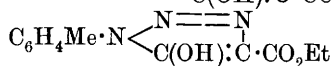
Desmotropic Compounds. OTTO DIMROTH (*Zeit. Elektrochem.*, 1905, 11, 137—139).—The author fully admits the weight of Gold-

schmidt's criticisms (this vol., i, 249). He points out, however, the fact that the velocity of the change of the enolic form of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate into the ketoic form is greater in solvents with small dissociating power ; for example, it is 10,000 times greater in chloroform solution than in aqueous solution. The change also occurs in the solid compound. It is therefore extremely probable that the change takes place within the undissociated molecule, and also that it has no connection with the formation of a hydrate.

T. E.

Desmotropic Compounds. II. OTTO DIMROTH (*Annalen*, 1905, 338, 143—182. Compare Abstr., this vol., i, 98).—The investigation of the desmotropic change of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate into methyl 1-phenyl-5-triazolone-4-carboxylate (*loc. cit.*) has now been extended to the corresponding *p*-bromophenyl and *p*-tolyl derivatives, the ethyl esters being used instead of the methyl

esters. The expressions $\text{C}_6\text{H}_4\text{Br}\cdot\text{N} \begin{smallmatrix} \text{N}=\text{N} \\ \diagdown \quad \diagup \\ \text{C}(\text{OH})\cdot\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ and



represent respectively the enolic forms of these compounds. The enolic forms are colourless, of marked acid character, whilst the ketonic forms are yellow and neutral. The former change into the latter very slowly in the solid state, immediately on melting, and in solution with a velocity depending on the nature of the solvent. The ketonic esters are the stable form. The tolyl compound is a weaker, and the *p*-bromophenyl a stronger, acid than the phenyl derivative ; the dissociation-constants are, respectively, tolyl, $100K = 1.0$; phenyl, $100K = 1.5$; and bromophenyl, $100K = 2.0$. The acids obtained from the esters are also desmotropic, the enolic acid being colourless and dibasic, and the ketonic yellow and monobasic. The enolic acid loses carbon dioxide, becoming converted into the triazole, but the ketonic acids yield respectively the *p*-bromoanilide and *p*-toluidide of glycollic acid.

The change of the enolic into the ketonic form is a unimolecular reaction. A table is given showing the relative values of the velocity constant *k* at 25° for the three hydroxytriazole derivatives.

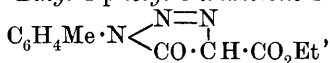
The velocity of the change increases *pari passu* with the increase of strength of the acid ; in all solvents, the phenyl derivative changes from 1.1 to 1.2 times more rapidly, and the bromophenyl from 4 to 5 times more rapidly than the tolyl compound. The velocity in all cases is smallest in water, and increases from methyl to ethyl alcohol and is greatest in acetone. Raising the temperature from 0° to 25° is accompanied by a great increase in the velocity in the ratio of 1 : 50 of the change in ethyl alcohol.

The proportion of enolic and ketonic forms present in equilibrium in methyl and ethyl alcohols has been estimated. In methyl alcohol, the proportion of enolic to ketonic form is, for the tolyl compound, 1/120, for the phenyl, 1/150, and for the bromophenyl, 1/555 ; in ethyl alcohol, the proportion is 1/230, 1/300 respectively for the two derivatives first mentioned. From these values, the velocity constant of

the change of the ketonic into the enolic form can be calculated. It is found that at 25° the velocity of this change is independent of the solvent and is the same for each of the three compounds, a fact which offers a remarkable contrast to the change of enol to ketone.

These results show that increase of the acidity of the enolic form is accompanied by an increase of the tendency to change into the ketonic form, a result in direct opposition to the behaviour of the di- and tri-ketones and to the desmotropy observed in the case of nitro-compounds.

[With H. STAHL.]—*Ethyl 1-p-tolyl-5-triazolone-4-carboxylate*,



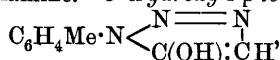
is prepared by warming an alcoholic solution of *p*-tolyl diazoimide and ethyl sodiomalonate and decomposing the sodium salt of the enolic form, which separates with hydrochloric acid. On warming the enolic ester under water, it is converted into the ketonic form. The latter crystallises in yellow needles melting at 98–99°, and dissolves only gradually in alkali hydroxides, becoming thereby converted into the enolic form, from which it is distinguished by giving no coloration with ferric chloride and not setting free iodine from a solution of potassium iodate and iodide. The corresponding enolic *ethyl 5-hydroxy-1-p-tolyl-1:2:3-triazole-4-carboxylate* is obtained in the form of the sodium salt by treatment of a suspension of the ketone in alcohol with sodium ethoxide; the salt forms a white, crystalline powder soluble in water with a neutral reaction. When agitated with aqueous hydrochloric acid at 0°, the free enolic ester is formed as a white, crystalline powder, which, when kept in a desiccator in the dark, changes into the ketone very slowly, about 1·5 per cent. in the course of a week. If heated slowly, the colour changes to yellow and the melting point becomes that of the ketone, 98–99°. If heated suddenly to 90°, it melts, but not if heated to 88°. After melting at 90°, it immediately solidifies again, being converted into the ketonic ester. It can readily be titrated by potassium hydroxide in the presence of phenolphthalein or by estimating the iodine set free from a mixture of potassium iodate and iodide. The *ammonium* salt is a soluble, and the *silver* salt an insoluble, white powder. The *aniline* salt, $\text{C}_{18}\text{H}_{20}\text{O}_3\text{N}_4$, prepared by mixing cold alcoholic solutions of the base and the enol, crystallises in plates melting at 102°; the *phenylhydrazine* salt is a crystalline powder melting at 124·5°; the *benzidine* salt, $\text{C}_{36}\text{H}_{38}\text{O}_8\text{N}_8$, is a powder melting at 129°; the *o-tolidine* salt, $\text{C}_{38}\text{H}_{42}\text{O}_6\text{N}_8$, a crystalline powder melting at 119·5°, and the *o-anisidine* salt, $\text{C}_{38}\text{H}_{42}\text{O}_8\text{N}_8$, a grey powder melting at 112°. On melting, all these salts decompose into the free base and the ketonic form.

Ethyl 5-methoxy-1-p-tolyl-1:2:3-triazole-4-carboxylate is prepared from the silver salt of the enolic ester and methyl iodide in ethereal suspension, and forms cubical crystals melting at 68–69°. The *benzoxy*-compound is prepared from the silver salt and benzoyl chloride in absolute ether, and crystallises in needles and in compact crystals melting at 117–120°.

5-Hydroxy-1-p-tolyl-1:2:3-triazole-4-carboxylic acid is prepared by heating the ketonic ester with concentrated aqueous sodium hydroxide,

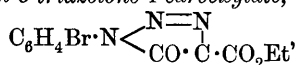
when the *di-sodium* salt, $C_{10}H_7O_3N_3Na_2$, of the enolic acid separates as a white, crystalline powder, easily soluble in water. The free acid, prepared by treatment of the sodium salt with hydrochloric acid at a low temperature, is a crystalline powder (with H_2O), melting and decomposing at $86-88^\circ$; it decomposes readily, losing carbon dioxide. The corresponding ketonic form, *1-p-tolyl-5-triazolone-4-carboxylic acid*,

$C_6H_4Me \cdot N \begin{smallmatrix} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH} \cdot \text{CO}_2\text{H} \end{smallmatrix}$ is obtained by keeping an ethereal solution of the enolic acid, and forms pale yellow, rhombic crystals sintering at 120° and melting at $175-180^\circ$; when heated, it gives a strong smell of carbilamine. *5-Hydroxy-1-p-tolyl-1:2:3-triazole*,



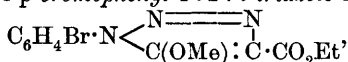
prepared by heating the enolic acid at 80° under water, crystallises in microscopic plates, melting and decomposing at 137° . When the ketonic acid is boiled with water, it quickly decomposes into glycollic-*p*-toluidide (m. p. 143°).

Ethyl 1-p-bromophenyl-5-triazolone-4-carboxylate,



prepared from *p*-bromophenyldiazoimide and sodium ethoxide, crystallises in yellow needles melting at 138.5° . The *sodium* salt of the corresponding enol ester is prepared from the ketone by treatment with sodium ethoxide, and is converted by dilute hydrochloric acid at a low temperature into the free *enolic* ester, a white, crystalline powder, which changes so rapidly into the ketonic ester that the melting point cannot be determined. The *ammonium* salt is a white, crystalline powder, sintering at 180° and melting and decomposing at $182-183^\circ$; the *silver* salt is a white, insoluble powder. The *aniline* salt crystallises in white needles melting at $114-115^\circ$, the *phenylhydrazine* salt forms yellow crystals melting at 125° . The *benzidine* salt is a white, crystalline powder, the *o-tolidine* salt crystallises in needles melting at $110-118^\circ$, and the *o-anisidine* salt in small crystals melting at $88-89^\circ$.

Ethyl 5-methoxy-1-p-bromophenyl-1:2:3-triazole-4-carboxylate,



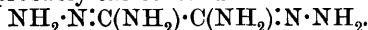
prepared from the silver salt, melts at 93° . The corresponding *benzoyloxy*-derivative crystallises in needles melting at 137° .

5-Hydroxy-1-p-bromophenyl-1:2:3-triazole-4-carboxylic acid is prepared by hydrolysing the ketonic ester with excess of sodium hydroxide, and then setting free the enolic acid from the di-sodium salt; it forms a white, crystalline powder with $2H_2O$, melting and decomposing at $96-100^\circ$. The *ketonic acid* is formed from the enol in ethereal solution, and crystallises in yellow needles melting and decomposing at 130° , the substance which is thus formed then melting at $207-208^\circ$. The enolic acid yields the corresponding *5-hydroxy-1-p-bromophenyl-1:2:3-triazole*, which forms small crystals, melting and decomposing at 124° . The ketonic acid yields, on the other hand, *glycollic-p-bromoanilide*-

$C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot OH$, which crystallises in needles melting at 180° .
K. J. P. O.

Bistriazole Compounds. ERICH L. RINMAN (*Arkiv Kemi, Min., Geol.*, 1904, 1, 221—263).—The author first gives an account of the bistriazole compounds already described and of the methods employed for preparing them.

The new bistriazole compounds described in the present paper have been obtained by means of cyanohydrazine (see Curtius, *Abstr.*, 1895, i, 29), which has probably the constitution



When this compound is treated with an acid anhydride or chloride, it yields a condensation product of the formula $C_2(NH_2)_2(:N \cdot NH \cdot CO \cdot R)_2$, and this, under the action of condensing agents, loses water and gives rise to a bistriazole compound. Condensation products containing different alkyl groups undergo conversion into bistriazole derivatives with varying degrees of ease and require, in some cases, acid condensing agents, and in others alkaline ones. The bistriazoles obtained form salts with both acids and bases, and all except phenylbistriazole yield well-defined crystalline platinichlorides of the type



Cyanohydrazine acts on ethyl chlorocarbonate, giving the compound $C_2(NH_2)_2(:N \cdot NH \cdot CO_2Et)_2$, which, when treated with dilute potassium hydroxide solution, loses alcohol and condenses to bishydroxytriazole.

The oxidation of bismethyl- or bisethyl-triazole in alkaline solution yields potassium bistriazolecarboxylate,



which yields an acetyl derivative of the constitution

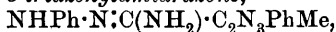


The author has synthesised cyanohydrazine by the action of hydrazine hydrate on dithio-oxamide, hydrogen sulphide being evolved and a practically quantitative yield of the cyanohydrazine being obtained.

On passing cyanogen into an aqueous solution of acetylhydrazide (Curtius, *Abstr.*, 1895, i, 32), dicyanoacetylhydrazide is obtained. This compound can be converted into bismethyltriazole by two methods: (1) on heating its alcoholic solution in a sealed tube with acetylhydrazide, it yields a compound which is identical with that obtained by the interaction of acetic anhydride and cyanohydrazine and which, when boiled with acetic anhydride, gives bismethyltriazole. (2) It may be first converted into a monotriazole derivative and then into a bistriazole compound.

Bis-1-phenyl-3-triazole, $C_2N_3HPh \cdot C_2N_3HPh$, prepared by treating with water the product of the interaction of cyanophenylhydrazine and formic acid, separates from acetic acid in crystals melting at $277-278^\circ$ and dissolving slightly in alcohol.

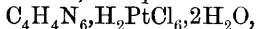
1-Phenyl-5-methyl-3-triazenylamidrazone,



obtained by acting with water on the product of the interaction of phenylmethyltriazenylamidoxime and an alcoholic solution of phenylhydrazine in a sealed tube, crystallises from alcohol in pale yellowish-brown prisms, which melt and decompose at 195° .

Bis-1-phenyl-5-methyl-3-triazole, $C_2N_3PhMe \cdot C_2N_3PhMe$, prepared by treating the preceding compound with acetic anhydride and acting on the product with dilute potassium hydroxide solution, separates in crystals which melt at $213-214^{\circ}$, but on subsequent heating, at $221-222^{\circ}$ (compare Bladin, Abstr., 1889, 138).

Bis-3-triazole, $C_4H_4N_6$, prepared by the action of water on the condensation product of cyanohydrazine and formic acid, sublimes without melting at temperatures above 325° and dissolves in both acids and alkalis and to some extent in water. The *potassium*, *sodium*, *ammonium*, *copper*, and *silver* salts were prepared and the *hydrochloride*, which crystallises in shining, white leaves and readily loses its hydrogen chloride in the air; the *platinichloride*,



separates in yellowish-red needles.

Bis-1-acetyl-3-triazole, $C_4H_2N_6Ac_2$, crystallises from a mixture of acetic acid and anhydride in spherical aggregates of white needles turning brown at about 225° .

Bis-5-methyl-3-triazole, $C_4H_2N_6Me_2$, separates from acetic acid in aggregates of small, white crystals, sublimes at above 325° , and dissolves readily in dilute mineral acids and to a slight extent in alcohol, water, or dilute acetic acid. The *potassium*, *sodium*, *ammonium* ($C_6H_{14}N_8$), and *silver* salts were prepared; the *hydrochloride*, $C_6H_8N_6 \cdot 2HCl$, crystallises in small, colourless prisms and the *platinichloride* ($+2H_2O$) in large, yellowish-red prisms.

Bis-1-acetyl-5-methyl-3-triazole, $C_4N_6Me_2Ac_2$, crystallises from alcohol in slender, white needles melting and decomposing at about 230° .

Bis-5-ethyl-3-triazole, $C_4H_2N_6Et_2$, prepared from cyanohydrazine and propionic anhydride, separates from acetic acid in nodular crystals, sublimes at above 325° , and dissolves readily in dilute mineral acids and to a slight degree in water or alcohol. The *potassium*, *sodium*, and *ammonium* salts were prepared; the *hydrochloride* forms stable, thick, semi-translucent needles and the *platinichloride* ($+2H_2O$) separates in large, reddish-yellow crystals readily soluble in concentrated or dilute hydrochloric acids.

Bis-1-acetyl-5-ethyl-3-triazole, $C_4N_6Et_2Ac_2$, crystallises from alcohol in shining, white needles, melts at $185-186^{\circ}$ and is decomposed by boiling water.

Bis-5-isopropyl-3-triazole, $C_4H_2N_6Pr^2$, prepared by heating the condensation product of diisopropylcyanohydrazine with sodium ethoxide in alcoholic solution, separates from alcohol in aggregates of small, colourless crystals, sublimes at above 325° , and dissolves readily in dilute mineral acids. The *potassium*, *sodium*, and *ammonium* salts were prepared; the *hydrochloride* forms aggregates of colourless crystals and the *platinichloride* separates from concentrated hydrochloric acid in large, reddish-yellow, anhydrous plates.

Bis-1-acetyl-5-isopropyl-3-triazole, $C_4N_6Pr^2Ac_2$, separates from alcohol in slender, white needles and melts at $200-202^{\circ}$.

Bis-5-phenyl-3-triazole, $C_4H_2N_6Ph_2$, crystallises from a mixture of acetic and concentrated hydrochloric acids in shining, microscopic needles, sublimes at above 325° , and dissolves slightly in acetic acid. The *potassium*, *sodium*, and *ammonium* salts were prepared; the *hydrochloride* ($+ 4H_2O$) forms microscopic needles decomposed by water.

Bis-1-acetyl-5-phenyl-3-triazole, $C_4N_6Ph_2Ac_2$, forms microscopic crystals with two rhombic surfaces and melting at $204-205^\circ$.

The condensation product of ethyl chlorocarbonate and cyanohydrazine (*vide supra*) crystallises from alcohol in microscopic, pointed needles which remain unchanged at 300° .

Bis-5-hydroxy-3-triazole, $C_4H_2N_6(OH)_2$, is obtained as a yellowish-white powder which is not changed at 325° .

Potassium bis-3-triazole-5-carboxylate, $C_4H_2N_6(CO_2K)_2 \cdot H_2O$, separates from water in shining, white needles.

Bis-3-triazole-5-carboxylic acid, $C_4H_2N_6(CO_2H)_2$, separates from acetic acid in microscopic crystals which remain unchanged at 325° . The *hydrochloride*, $C_4H_2N_6(CO_2H)_2 \cdot 2HCl$, crystallises from a mixture of acetic and dilute hydrochloric acids in almost colourless leaflets. The *acetyl* derivative was prepared and the *benzoyl* derivative, which crystallises from water in pale greyish-yellow, three-sided prisms melting at $208-210^\circ$.

Dicyanoacetylhydrazide, $NHAc \cdot N:C(CN) \cdot NH_2$, crystallises from alcohol in yellowish-brown leaves melting and decomposing at $204-205^\circ$.

Diacetylcyanohydrazine, $NHAc \cdot N:C(NH_2) \cdot C(NH_2) \cdot N:NHAc$, crystallises from water in faintly translucent needles.

Dicyanoacetylhydrazideamidoxime, $NHAc \cdot N:C(NH_2) \cdot C(NH_2) \cdot NOH$, crystallises from water with H_2O in thin rods resembling mica which melt and decompose at 202° .

Methyltriazoleamidoxime, $C_2HN_3Me \cdot C(NH_2) \cdot N \cdot OH$, prepared by heating the preceding compound in a sealed tube with an alcoholic solution of sodium ethoxide, crystallises from water in colourless needles melting and decomposing at 212° .

Dicyanopropionylhydrazide, $COEt \cdot NH \cdot N:C(CN) \cdot NH_2$, separates from alcohol in a nodular, crystalline mass.

Dicyanobenzoylhydrazide, $NHBz \cdot N:C(CN) \cdot NH_2$, prepared by passing cyanogen into an aqueous solution of benzoylhydrazide, crystallises from alcohol in spherical aggregates of slender, yellowish-white needles melting and decomposing at $194-195^\circ$.
T. H. P.

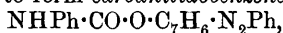
Hydroxyazo-compounds. HEINRICH GOLDSCHMIDT and OSCAR LÖW-BEER (*Ber.*, 1905, 38, 1098—1113. Compare Abstr., 1890, 614; 1891, 1209; 1892, 974; McPherson, Abstr., 1896, i, 27; 1900, i, 123; Jacobson and Hönigsberger, Abstr., 1904, i, 205; Borsche, Abstr., 1904, i, 1056).—Phenylcarbimide reacts with *o*- and *p*-hydroxyazo-compounds to form carbamates which are insoluble in dilute alkali hydroxides. The carbamates derived from the *o*-hydroxyazo-compounds are reduced to hydrazo-compounds, which undergo the benzidine change, yielding diacid bases which are insoluble in dilute alkali hydroxides. These facts militate against the quinonehydrazone constitution for the hydroxyazo-compounds.

Carbanilido-*p*-hydroxyazobenzene is formed by the action of

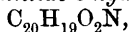
phenylcarbimide on *p*-hydroxyazobenzene at the ordinary temperature; it crystallises in yellow needles and is now found to melt at 157°.

Carbo-p-toluidido-p-hydroxyazobenzene, $C_7H_7 \cdot NH \cdot CO \cdot O \cdot C_6H_4 \cdot N_2Ph$, formed from *p*-tolylcarbimide and *p*-hydroxyazobenzene, crystallises in yellow leaflets, melts at 170.5°, and is reduced by zinc dust and acetic acid in alcoholic solution to *carbo-p-toluidido-p-hydroxyhydrazobenzene*, $C_7H_7 \cdot NH \cdot CO \cdot O \cdot C_6H_4 \cdot NH \cdot NPh$, which crystallises in small, colourless prisms, melts at 171°, and is insoluble in dilute alkali hydroxides. *Carbo-o-toluidido-p-hydroxyazobenzene* crystallises in slender, yellow needles, melts at 152°, and is reduced to *carbo-o-toluidido-p-hydroxyhydrazobenzene*, which crystallises in colourless needles and melts at 150°.

Benzeneazo-*p*-cresol reacts slowly with phenylcarbimide at the ordinary temperature to form *carbanilidobenzeneazo-p-cresol*,



which decomposes into its generators when recrystallised from hot benzene; it is obtained by oxidation of the hydrazo-compound with mercuric oxide in ethereal solution in orange-red needles melting at 139°. *Carbanilidobenzenehydrazo-p-cresol* crystallises in nodular aggregates of colourless needles, melts at 157°, is insoluble in dilute alkali hydroxides, and when treated with concentrated hydrochloric acid in alcoholic solution yields *carbanilido-5-hydroxy-2-methylbenzidine*,



which crystallises from benzene, melts at 143—145°, and when boiled with aqueous sodium hydroxide is hydrolysed to aniline and a *substance* which is precipitated by carbon dioxide, but is soluble in mineral acids. The *hydrochloride*, $C_{20}H_{19}O_2N_3 \cdot 2HCl$, crystallises in long, slender, colourless needles and melts at 291°.

Carbanilido-p-tolueneazo-p-cresol crystallises in orange-coloured needles, melts at 124°, and is reduced by zinc dust in alcoholic solution to *carbanilido-p-toluenehydrazo-p-cresol*, which crystallises in white needles and melts at 165°.

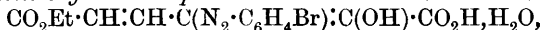
Carbanilido-m-chlorobenzeneazo-p-cresol crystallises in slender, orange-coloured needles, melts at 135—136°, and is soluble in the ordinary organic solvents. *Carbanilido-m-chlorobenzenehydrazo-p-cresol* crystallises in white needles, melts at 140°, is insoluble in cold dilute alkali hydroxides, and when treated with hydrochloric acid in alcoholic solution undergoes the benzidine change. The *base*, $C_{20}H_{16}O_2N_3Cl$, contains water of crystallisation, commences to sinter at 70°, and melts and decomposes at 140°; when anhydrous, it crystallises in white needles, melts at 134°, and, when boiled with aqueous sodium hydroxide, yields aniline and a *product* which is soluble in dilute alkali hydroxides and in dilute acids.

When reduced with zinc dust and acetic acid in alcoholic solution, the benzoyl derivative, obtained by the action of benzoic chloride on β -naphthaquinonephenylhydrazone or by the action of α -benzoylphenylhydrazine on β -naphthaquinone, yields β -benzenehydrazo- α -benzoylnaphthol, which crystallises in slender, colourless needles, melts and becomes red at 170°, is insoluble in dilute alkali hydroxides, and when treated with sodium hydroxide in alcoholic solution yields β -naphthaquinonephenylhydrazone.

G. Y.

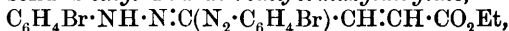
Azo-derivatives of Ethyl Oxalocrotonate. BERNHARDT PRAGER (*Annalen*, 1905, 338, 360—392).—In order to study the resemblances and differences between a series of alternately singly and doubly linked carbon atoms in an open chain and in a closed ring, the formation of azo-derivatives from a phenol has been compared with their formation from unsaturated hydroxy-compounds. Diethyl oxalocrotonate (Lapworth, *Trans.*, 1901, 79, 1276), $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\text{:CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, has been chosen as offering a series of CH groups related to an OH group, as are the ortho- and para-positions in phenol. It has been found that this compound yields readily both an azobenzene derivative and a dis-azo-derivative, thus: $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\text{:C}(\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ and $\text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\text{:C}(\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})\cdot\text{CH}\text{:C}(\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})\cdot\text{CO}_2\text{Et}$; it is seen that the monoazobenzene derivative is analogous to the *o*-phenolazobenzene, and not to the *para*-derivative, which is mainly formed in the case of phenol. Since diazobenzenes will not couple with ethyl crotonate or ethyl sorbate, the power to combine with diazobenzene is not due to the double bindings but to the hydroxyl group.

Diethyl bis-p-bromobenzenediazo-oxalocrotonate is obtained by adding a solution of *p*-bromobenzenediazonium chloride to a solution of ethyl oxalocrotonate in a dilute solution of sodium carbonate, as an orange-red solid, which is purified by repeated extraction with small quantities of methyl alcohol and subsequent recrystallisation from alcohol; it forms crystals melting at 160° . The yellow alkaline mother liquor, from which the substance last mentioned separates, yields on acidification the *monoethyl ester of p-bromobenzenediazo-oxalocrotonic acid*,



which crystallises in yellow needles, melting and decomposing at $122\text{--}123^\circ$. When 2 mols. of the *p*-bromodiazobenzene are used instead of one for each mol. of oxalocrotonate, no acid is formed and a somewhat better yield of the bis-azo-compound is obtained.

When the diazo-solution is added to an ammoniacal solution of the oxalocrotonate, a red precipitate separates, leaving a colourless mother liquor; this solid is *ethyl 4:4'-dibromoformazylacrylate*,



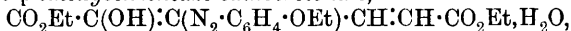
which crystallises in needles melting at $150\text{--}151^\circ$. If a solution of benzenediazonium instead of *p*-bromobenzenediazonium chloride is used, the corresponding *ethyl formazylacrylate*, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_4$, is obtained as red needles melting at 128° . In both cases, alteration of the relative proportions of diazonium salt and oxalocrotonate does not affect the formation of the formazyl.

Diethyl p-bromobenzenediazo-oxalocrotonate is obtained when an acid solution of *p*-bromobenzenediazonium chloride in alcohol is added to an alcoholic solution of the oxalocrotonate; it crystallises in pale yellow prisms or needles melting at $125\text{--}126^\circ$, and dissolves very slowly in alkaline solutions. By use of excess of the diazonium salt, no dibenzenediazo-derivative was formed, but it is obtained if the monobenzenediazo-derivative is treated with *p*-bromodiazobenzene in acetic acid solution.

Since both the monoethyl *p*-bromobenzenediazo-oxalocrotonate and the diethyl ester, when treated with *p*-bromodiazobenzene in ammoniacal solution, yield the same ethyl dibromoformazylacrylate, it follows that

the benzeneazo-group is attached to the same carbon atom in the two compounds.

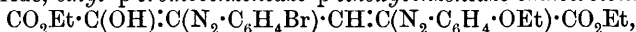
Diethyl p-ethoxybenzeneazo-oxalocrotonate,



is prepared from *p*-ethoxydiazobenzene and the oxalocrotonate in alcoholic solution, and crystallises in orange-yellow prisms melting at 85—86°. When treated with *p*-bromodiazobenzene in acetic acid solution, it is converted into *ethyl p-ethoxybenzeneazo-p-bromobenzeneazo-oxalocrotonate*,

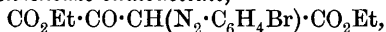


which crystallises in orange prisms melting at 160—161°; the isomeride, *ethyl p-bromobenzeneazo-p-ethoxybenzeneazo-oxalocrotonate*,



is prepared from *p*-ethoxydiazobenzene and ethyl *p*-bromobenzeneazo-oxalocrotonate, and forms orange crystals melting at 169—170°, and is somewhat less soluble in all solvents than the isomeride.

Ethyl p-bromobenzeneazo-oxaloacetate,



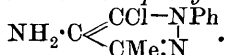
prepared from ethyl oxaloacetate and *p*-bromodiazobenzene in acetic acid solution, crystallises in yellow prisms melting at 93—94°, and is soluble in alkalis on warming. The corresponding formazyl, *ethyl 4:4'-dibromoformazylformate*, $\text{C}_6\text{H}_4\cdot\text{Br}\cdot\text{NH}\cdot\text{N}\cdot\text{C}(\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{Br})\cdot\text{CO}_2\text{Et}$, is obtained by carrying out the coupling in the presence of ammonia, and crystallises in red needles melting at 158—160°; it is also formed from the ethyl *p*-bromobenzeneazo-oxaloacetate and *p*-bromodiazobenzene in acetic acid solution.

K. J. P. O.

Azo-compounds of Phenylpyrazoles and their Halogen and Thio-derivatives. AUGUST MICHAELIS (*Annalen*, 1905, 338, 183—235. Compare Abstr., 1904, i, 124).—A number of azopyrazoles are described which have been prepared from the corresponding benzeneazopyrazolones.

[With RICHARD LEONHARDT and KARL WAHLE.]—5-Chloro-1-phenyl-3-methylpyrazole-4-azobenzene, $\text{N}_2\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{CCl-NPh} \\ \text{CMe:N} \end{smallmatrix}$, is prepared from

Knorr's phenylmethylpyrazoloneazobenzene by treatment with phosphorus oxychloride under pressure at 100°, and crystallises in slender, yellow needles melting at 109°; it is reconverted into the original substance by alcoholic potassium hydroxide, and with acid reducing agents yields 5-chloro-4-amino-1-phenyl-3-methylpyrazole,

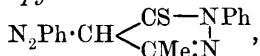


The azo-compound gives with alcoholic silver nitrate an *additive compound*, $(\text{C}_{16}\text{H}_{13}\text{N}_4\text{Cl})_2\cdot\text{AgNO}_3$, which crystallises in yellow needles, melting at 132°, and is decomposed by hydrochloric acid. 5-Iodo-1-phenyl-3-methylpyrazole-4-azobenzene is obtained by the action of alcoholic potassium iodide on the chlorine compound and crystallises in reddish-yellow needles melting at 129°.

1-Phenyl-3-methylpyrazole-4-azobenzene, $\text{N}_2\text{Ph}\cdot\text{C}\begin{smallmatrix} \text{CH-NPh} \\ \text{CMe:N} \end{smallmatrix}$, is pre-

pared by reducing the azochloro- or azoiido-pyrazole with zinc dust and sodium hydroxide in alcoholic solution, and crystallises in reddish-yellow leaflets melting at 126° ; it yields an unstable *hydrochloride* crystallising in red needles melting and decomposing at 114° .

1-Phenyl-3-methyl-5-thiopyrazolone-4-azobenzene,



is prepared by heating the chloroazopyrazole with sulphide of potassium or sodium in alcoholic solution, a salt of the thio-compound being first obtained; the substance crystallises in dark red needles melting at 97° , behaves as a weak base, and is soluble in alkali hydroxides, but not in carbonates; it is reduced to a colourless substance by acid reducing agents. The *mercury mercaptide* is obtained by adding mercuric oxide to a boiling solution of the azothiopyrazolone in toluene, and crystallises in brick-red needles melting at 228° . The *mercurichloride*, $\text{N}_2\text{Ph} \cdot \text{C} \begin{array}{l} \text{C}(\text{S} \cdot \text{HgCl}) \cdot \text{NPh} \\ \text{CMe} = \text{N} \end{array}$, pre-

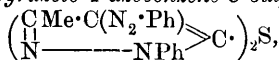
pared by mixing a hot alcoholic solution of mercuric chloride and the azothiopyrazolone, crystallises in yellow needles melting at 217° .

5-Thiomethyl-1-phenyl-3-methylpyrazole-4-azobenzene, prepared by treating the azothiopyrazolone with methyl iodide in the presence of alcoholic potassium hydroxide, crystallises in reddish-yellow needles melting at 63° and is readily oxidised by permanganate to the cor-

responding *sulphone*, $\text{N}_2\text{Ph} \cdot \text{C} \begin{array}{l} \text{C}(\text{SO}_2 \text{Me}) \cdot \text{NPh} \\ \text{CMe} = \text{N} \end{array}$, which crystallises in

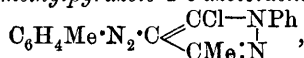
reddish-yellow needles melting at 156° . The 5-thioethyl-pyrazole, prepared in like manner to the methyl derivative, crystallises in reddish-yellow needles melting at 71° ; it can also be obtained from 5-chloro-1-phenyl-3-methyl-4-azobenzene and sodium mercaptide. The 5-thiophenyl-pyrazole is obtained from the chloroazopyrazole and thiophenol in the presence of sodium ethoxide, and crystallises in yellowish-red plates or prisms melting at 115° ; the *sulphone*, obtained from it by oxidation with permanganate in acetic acid solution, forms scarlet crystals melting at 145° . When the sodium salt of the azothiopyrazolone is shaken with benzoyl chloride, the *thiobenzoate* is formed as red needles melting at 127° . Monochloroacetic acid reacts with an alkaline solution of the azothiopyrazolone giving a 4-benzeneazo-1-phenyl-3-methylpyrazole-5-thioglycollic acid, $\text{N}_2\text{Ph} \cdot \text{C} \begin{array}{l} \text{C}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{NPh} \\ \text{CMe} = \text{N} \end{array}$, crystallising in pale yellow needles melting at 166° ; its *silver* salt crystallises in red needles melting and decomposing at 193° .

1-Phenyl-3-methylpyrazole-4-azobenzene-5-sulphide,

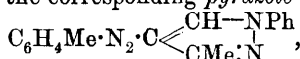


is prepared by heating together molecular proportions of 5-chloroazopyrazole and 4-azothiopyrazolone at 100° , and crystallises in pale reddish-yellow needles melting at 86° ; the corresponding *disulphide* is obtained by the action of iodine on a solution of the mercury salt of azothiopyrazolone in toluene, and crystallises in dark yellow, rhombic prisms melting at 115° .

5-Chloro-1-phenyl-3-methylpyrazole-4-o-azotoluene,

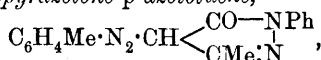


prepared by the action of phosphorus oxychloride on the corresponding pyrazolone, crystallises in yellow needles melting at 94° . 1-Phenyl-3-methyl-5-pyrazolone-o-azotoluene is prepared by adding a solution of o-toluenediazonium chloride in hydrochloric acid to a solution of phenylmethylpyrazolone in acetic acid; it crystallises in red needles melting at 185° . The chloro-compound is reduced by zinc dust and sodium hydroxide to the corresponding pyrazole-o-azotoluene,



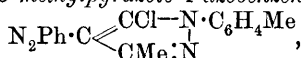
which forms golden-yellow leaflets melting at 91° ; the hydrochloride crystallises in red needles. 5-Thiol-1-phenyl-3-methylpyrazolone-4-o-toluene crystallises in dark red needles melting at 136° .

1-Phenyl-3-methylpyrazolone-p-azotoluene,



is prepared in similar manner to the corresponding ortho-compound crystallises in red needles melting at 141° , and yields with phosphorus oxychloride the 5-chloro-compound, which forms yellow needles melting at 118° . On reduction, it gives the corresponding pyrazole, which crystallises in yellow leaflets melting at 84° . The thiopyrazolone crystallises in dark red needles melting at 123° .

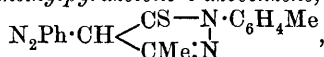
5-Chloro-1-p-tolyl-3-methylpyrazole-4-azobenzene,



prepared by the action of phosphorus oxychloride on 1-p-tolyl-3-methyl-5-pyrazolone-4-azobenzene, crystallises in yellow needles melting at 107° . When oxidised by chromic acid in the presence of sulphuric acid, it is converted into 5-chloro-4-benzeneazo-3-methylpyrazole-1-p-benzoic acid, $\text{N}_2\text{Ph}\cdot\text{C} \begin{array}{l} \text{CCl}-\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \\ \text{CMe}:\text{N} \end{array}$, which is a

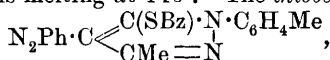
brown, insoluble powder. The chloropyrazole yields an additive compound with silver nitrate, $(\text{C}_{17}\text{H}_{15}\text{N}_4\text{Cl})_2\cdot\text{AgNO}_3$, which crystallises in yellow needles melting at $193-194^\circ$. 1-p-Tolyl-3-methylpyrazole-4-azobenzene, prepared by reducing the chloro-compound with zinc dust and sodium hydroxide, crystallises in pale yellow needles melting at 83° ; its hydrochloride is colourless and unstable.

5-Thio-1-p-tolyl-3-methylpyrazolone-4-azobenzene,

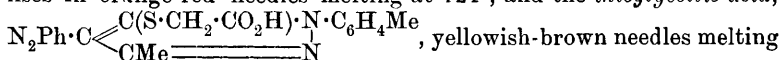


prepared from the chloropyrazole, crystallises in dark red needles melting at 116° , and when warmed with dilute nitric acid is converted into 5-nitro-1-p-tolyl-3-pyrazole-4-azobenzene, which crystallises in dark red needles melting at 132° and is insoluble in acids or alkali hydroxides. The mercury mercaptide crystallises in yellowish-red needles melting at 226° , and the mercurichloride, $\text{N}_2\text{Ph}\cdot\text{C} \begin{array}{l} \text{C}(\text{S}\cdot\text{HgCl})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me} \\ \text{CMe}=\text{N} \end{array}$, in

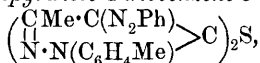
yellow needles melting at 236°. The *thiomethyl ether* forms dark yellow crystals melting at 82° and the *thioethyl ether* yellow crystals melting at 61° and the *thiophenyl ether* red prisms or plates melting at 108°, which, when oxidised, is converted into the *phenylsulphone* crystallising in reddish-yellow prisms melting at 146°. The *thiobenzoate*,



obtained from an alkaline solution by use of benzoyl chloride, crystallises in orange-red needles melting at 121°, and the *thioglycollic acid*,

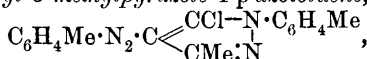


at 159°. Its *barium* salt forms pale yellow needles decomposing at 230°. 1-p-Tolyl-3-methylpyrazole-4-azobenzene-5-sulphide,



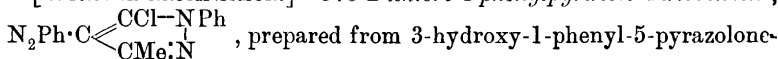
prepared from the chloropyrazole, crystallises in yellow needles melting at 106°.

5-Chloro-1-p-tolyl-3-methylpyrazole-4-p-azotoluene,

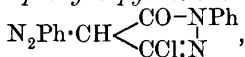


prepared in the usual manner, crystallises in yellow needles or leaflets melting at 155–156°, and on reduction yields the corresponding *pyrazole*, which forms dark yellow leaflets melting at 121°; its *hydrochloride* crystallises in red, unstable needles. 5-Thio-1-p-tolyl-3-methylpyrazolone-4-p-azotoluene, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2\cdot\text{CH}\begin{array}{l} \text{CS}-\text{N}\cdot\text{C}_6\text{H}_4\text{Me} \\ \text{CMe}:\text{N} \end{array}$, crystallises in lustrous, dark red leaflets melting at 174°.

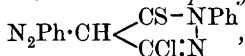
[With HEINRICH SIMON.]—3:5-Dichloro-1-phenylpyrazole-4-azobenzene,



the chlorine in position 5 being in all reactions the more easily replaced; the pyrazolone crystallises in purplish-red needles melting at 164°, and can also be prepared from 3-chloro-1-phenyl-5-pyrazolone and benzenediazonium chloride. 3-Chloro-1-phenylpyrazole-4-azobenzene is obtained by reduction of the dichloro-compound, and crystallises in yellow needles melting at 140°. 3-Chloro-5-thio-1-phenylpyrazolone-4-azobenzene,

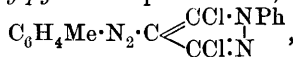


the chlorine in position 5 being in all reactions the more easily replaced; the pyrazolone crystallises in purplish-red needles melting at 164°, and can also be prepared from 3-chloro-1-phenyl-5-pyrazolone and benzenediazonium chloride. 3-Chloro-1-phenylpyrazole-4-azobenzene is obtained by reduction of the dichloro-compound, and crystallises in yellow needles melting at 140°. 3-Chloro-5-thio-1-phenylpyrazolone-4-azobenzene,



is prepared from the dichloro-compound and sodium or ammonium sulphide, and crystallises in reddish-brown needles melting at 138°.

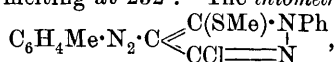
3:5-Dichloro-1-phenylpyrazole-4-p-azotoluene,



prepared in a manner similar to that described above, crystallises in

needles melting at 112° . When warmed with potassium iodide solution on the water-bath, 3-chloro-5-iodo-1-phenylpyrazole-4-p-azotoluene is obtained as orange-yellow leaflets melting at 143° . On treatment with alcoholic potassium hydroxide, the dichloro-compound yields 3-chloro-1-phenyl-5-pyrazolone-4-p-azotoluene, crystallising in red needles which melt at 85° . The corresponding 3-chloro-1-phenylpyrazole-4-p-azotoluene crystallises in lemon-yellow needles melting at 106° . 3-Chloro-5-thio-1-phenylpyrazolone-4-p-azotoluene crystallises in needles melting at 146° . 3-Bis-5-thio-1-phenylpyrazolone-4-p-azotoluene, prepared from the compound last mentioned by prolonged heating with an alkali, forms dark red crystals melting at 232° . The mercurichloride,

$C_6H_4Me \cdot N_2 \cdot C \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} C(S \cdot HgCl) \cdot NPh \\ CCl = N \end{smallmatrix}$, obtained when the corresponding thio-pyrazolone is treated with alcoholic mercuric chloride, crystallises in pale yellow needles melting at 232° . The thiomethyl-pyrazole,



prepared from the chlorothiopyrazolone and methyl iodide in the presence of alcoholic potassium hydroxide, crystallises in golden-yellow leaflets melting at 109° , and is oxidised to the corresponding sulphone by permanganate in acetic acid solution; the latter crystallises in yellow needles melting at 152° . The thioethyl-pyrazole crystallises in golden-yellow needles melting at 112° . The thiobenzoate,

$C_6H_4Me \cdot N_2 \cdot C \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} C(SBz) \cdot NPh \\ CCl = N \end{smallmatrix}$, crystallises in yellowish-red needles melting at 125° . 1-Phenyl-3-chloropyrazole-4-p-azotoluene-5-sulphide is prepared by heating a mixture of 3:5-dichloro-1-phenyl-4-p-azotoluene and the chlorothiopyrazolone and crystallises in yellow needles melting at 180° .

[With JOHANN BEHRENS.]—The azo-compounds of 1-phenyl-5-methyl-3-pyrazolone are prepared in the usual manner; 1-phenyl-5-

methyl-3-pyrazolone-4-azobenzene, $N_2Ph \cdot C \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} CMe \cdot NPh \\ CO - NH \end{smallmatrix}$, crystallises in

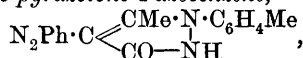
dark yellow leaflets or needles melting at $99-100^{\circ}$; its sodium salt is a red, crystalline powder melting at 207° , and its hydrochloride forms red needles melting at $147-149^{\circ}$. The benzenesulphonyl derivative,

$N_2Ph \cdot C \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} CMe \cdot NPh \\ C(SO_3Ph) \cdot N \end{smallmatrix}$, prepared by shaking an alkaline solution of

the azopyrazolone with benzenesulphonic chloride, crystallises in yellow needles melting at 132° . With phosphorus oxychloride, the azopyrazolone yields 3-chloro-1-phenyl-5-methylpyrazole-4-azobenzene,

$N_2Ph \cdot C \begin{smallmatrix} \swarrow \\ \searrow \end{smallmatrix} \begin{smallmatrix} CMe \cdot NPh \\ CCl = N \end{smallmatrix}$, which crystallises in yellow needles melting at 90° .

1-p-Tolyl-5-methyl-3-pyrazolone-4-azobenzene,



crystallises in brownish-yellow leaflets melting at 169° , and the corresponding o-tolyl derivative in yellowish-brown needles melting at

130°. The *sodium* salts of both compounds are red, crystalline powders. The *hydrochloride* of the *o*-tolyl compound is easily, but that of the *p*-tolyl compound sparingly, soluble; both form red needles. The *benzenesulphonyl* derivative of the *p*-tolyl compound crystallises in yellow needles melting at 112°, and that of the *o*-tolyl compound in yellow needles melting at 113°. 3-Chloro-1-*p*-tolyl-5-methylpyrazole-4-azobenzene, prepared by the action of phosphorus oxychloride on the 3-pyrazolone, forms pale red crystals melting at 103°. K. J. P. O.

Diazoamino-compounds derived from Diphenylamine and the Homologues of Aniline and the Naphthylamines. LÉO VIGNON and ADOLPHE SIMONET (*Compt. rend.*, 1905, 140, 788—790. Compare Abstr., 1904, i, 637, 1065).—The compound, $\text{NPh}\cdot\text{N}\cdot\text{NPh}_2$, obtained by diazotising aniline in presence of diphenylamine has been already described. The three toluidines, three xylidines, and the two naphthylamines have now been treated in a similar manner. The substance obtained from *o*-toluidine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{NPh}_2$, is a fairly stable oil of a red colour, very soluble in alcohol and ether, insoluble in water.

The *m*-toluidine derivative is a reddish-brown powder which crystallises readily from alcohol and decomposes at 135—140°. From *p*-toluidine, an unstable, reddish-brown oil is obtained which gives off nitrogen at the ordinary temperature.

From 1:2:3-xylidine, an oil is obtained which solidifies after several days, then melts at 100—110°, and decomposes at 125°. No definite products were obtainable from 1:2:4- and 1:4:3-xylidines. When α -naphthylamine is diazotised in presence of diphenylamine, the latter takes no part in the reaction. If α -naphthalenediazonium chloride is first prepared and treated with diphenylamine in alcoholic solution, a dark-coloured oil is obtained which is probably diphenylaminodiazonaphthalene. It gives off nitrogen and decomposes according to the equation $\text{C}_{10}\text{H}_7\text{N}\cdot\text{N}\cdot\text{NPh}_2 + \text{H}_2\text{O} = \text{C}_{10}\text{H}_7\cdot\text{OH} + \text{NHPh}_2 + \text{N}_2$. β -Naphthylamine behaves in a similar manner to the α -compound. The three monoaminophenols, *o*-aminobenzoic acid, and *o*-aminosalicylic acid do not yield diphenylaminodiaz-derivatives under the conditions described.

H. M. D.

Action of Chloroform on Proteids. E. S. EDIE (*Thompson, Yates, and Johnston Lab. Rep., Liverpool*, 1905, 6, 195—200).—The proteids investigated were those of serum and hæmoglobin, in reference to the work of Moore and Roaf (see this vol., ii, 272). The compound of chloroform and hæmoglobin is less stable than carboxyhæmoglobin. When sufficient chloroform is added to produce precipitation, the amount of chloroform found in the precipitate is constant. In the case of the serum proteids also, the amount of chloroform is fairly constant.

W. D. H.

A Globulin occurring in the Chestnut. WILLIAM E. BARLOW (*J. Amer. Chem. Soc.*, 1905, 27, 274—276).—A globulin has been obtained from the edible Spanish chestnut (*Castanea vesca*) by extraction with 10 per cent. sodium chloride solution; this, when dry, forms a grey powder, and under certain conditions separates as minute plates, bounded by three curved edges. The proteid is insoluble

in water, but is readily soluble in 10 per cent. sodium chloride solution, and is reprecipitated by ammonium sulphate, dilute hydrochloric acid, or acetic acid.

When a saline solution of the globulin is heated, it becomes opalescent at 74—75°, and is only partially precipitated on boiling; on adding a trace of hydrochloric acid to the hot solution, however, complete precipitation of the proteid takes place. In most of its reactions, this proteid resembles corylin, the globulin of the filbert, but differs from it in its temperature of coagulation and its precipitation limits with ammonium sulphate. The substance is probably not identical with any of the vegetable proteids previously isolated and is provisionally termed *castanin*. E. G.

Hydrolysis of Proteids. II. Gelatin. ZDENKO H. SKRAUP (*Monatsh.*, 1905, 26, 243—264. Compare Abstr., 1904, i, 538, 594; Siegfried, Abstr., 1903, i, 586).—Gelatin was hydrolysed by 12·5 per cent. hydrochloric acid at 39° for 12 days and the products isolated by addition of phosphotungstic acid, filtration of the amorphous precipitate, and evaporation of the filtrate.

On recrystallisation of the amorphous precipitate, a small amount of a crystalline phosphotungstate was obtained. The least soluble part of this yielded an acid, $C_{12}H_{25}O_{10}N_5$, which crystallises in long, thin, microscopic prisms, melts at 251—253°, and is easily soluble in hot water. The ammonium salt crystallises in microscopic plates; the copper salt, $C_{12}H_{19}O_{10}N_5Cu_3 \cdot 5H_2O$, forms long, blue prisms and loses $3H_2O$ at 130°. The moderately soluble part of the phosphotungstate formed stellate aggregates of slender needles and is probably Siegfried's glutokyrine phosphotungstate. The most soluble fraction of the phosphotungstate yielded diaminoglutaric acid. The filtrate from the amorphous precipitate yields glycine, diaminoglutaric acid, and an acid, $C_4H_7O_4N$, which decomposes without melting at 220° and forms a bluish-green copper salt. Aminohydroxysuccinic, diaminodihydroxy-suberic, and caseanic acids were not found amongst the hydrolysis products.

Glycine and diaminoglutaric acid, which are found in gelatin in much larger quantity than in casein, form a salt, $(C_2H_4O_2N)_2 \cdot C_5H_{10}O_4N_2$, which crystallises in microscopic prisms and melts and decomposes at 238—239°. G. Y.

Thymonucleic Acids. II. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1905, 43, 402—405. Compare Abstr., 1904, i, 837).—The results obtained by the hydrolysis of copper thymonucleate with various reagents are tabulated as follows, when the total nitrogen = 100.

Nitrogen in form of	Hydrolytic agent.		
	Hydriodic acid.	Sulphuric acid.	Hydrochloric acid and stannous chloride.
Ammonia	7·00	5·20	16·08
Humin	11·54	6·58	—
Guanine	3·61	10·07	3·15
Adenine ..	13·45	16·39	4·76
Cytosine	11·45	11·47	10·15
Thymine	15·88	13·11	11·91

The results indicate that sulphuric acid is the best hydrolytic agent, as it produces less complex decomposition. J. J. S.

Spectroscopic Study of Oxyhæmoglobin. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, 140, 685—687).—It has been found that the absorption spectrum of aqueous solutions of crystallised oxyhæmoglobin is altered on the addition of certain substances to the solutions.

The absorption band ($\lambda = 634$) is particularly sensitive, and the substances which displace or suppress this band are such as are usually regarded as having no action on the colouring matter of the blood. Sodium chloride in eight per cent. solution suppresses the band, and under certain conditions causes a thin band at $\lambda = 597$ to make its appearance. The alkali fluorides and hydrofluoric acid displace the band to the position $\lambda = 612$. The free acid produces this effect in very dilute solution, and is still more active at 38° than at 20° . Potassium chloride, bromide, and iodide have no action, and this is also the case for sodium bromide and iodide. The absorption band is suppressed by the alkalis and by sodium hydrogen carbonate, but not by dilute solutions of acids such as acetic and carbonic. It is intensified by alkali sulphates and magnesium sulphate.

H. M. D.

Modification of the Spectrum of Methæmoglobin under the Action of Sodium Fluoride. JULES VILLE and EUGÈNE DERRIEN (*Compt. rend.*, 1905, 140, 743—744).—The addition of a freshly prepared solution of sodium fluoride to a solution of methæmoglobin or methæmoglobinised blood causes the band in the red having its centre at $\lambda = 633$, characteristic of methæmoglobin, to disappear, whilst a new band is formed, having its centre at $\lambda = 612$. The same results have been obtained with blood methæmoglobinised by means of potassium ferricyanide, sodium nitrite, or hydrogenised palladium, with solutions of oxyhæmoglobin partially methæmoglobinised by spontaneous change, or with solutions of crystallised methæmoglobin. The change in the spectrum of oxyhæmoglobin observed by Piettre and Vila (preceding abstract) was probably due to a partial methæmoglobinisation of the colouring matter of the blood.

M. A. W.

Colouring Matter of Blood. IV. H. GOLDMANN and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, 43, 415—416).—Hæmopyrrole readily couples with an aqueous solution of benzenediazonium chloride, yielding an *azo-dye* which crystallises in brown needles melting at 241.5° . It is sparingly soluble in ether, toluene, boiling dilute hydrochloric acid, or alkali hydroxides, but dissolves readily in alcohol, yielding cherry-red solutions, in chloroform, or in concentrated sulphuric acid to bluish-violet solutions. J. J. S.

Colouring Matter of Blood. III. JOZEF BURACZEWSKI and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, 43, 410—414).—Attempts have been made to synthesise hæmopyrrole (Nencki and Zaleski, *Abstr.*, 1901, i, 434; Küster, *ibid.*, 1902, i, 845; Küster and Hass, *ibid.*, 1904, i, 647) by distilling α -methyl- β -propylmaleinimide

(Abstr., 1904, i, 648) with zinc dust in an atmosphere of hydrogen. After exposure to the air, a reddish-brown dye was obtained, which was soluble in alcohol and closely resembled urobilin.

Synthetical methylmalic acid has been resolved into its optically active components by means of strychnine, the salt of which with the *d*-acid is sparingly soluble. The *d*-acid crystallises from ethyl acetate, melts at 108—109°, and has $[\alpha]_D + 22.83^\circ$ at 20° ($c = 1.5$).

The hæmin crystals obtained by means of propionic acid (*Bull. Acad. Sci. Cracow*, 1904, 224) are crystallographically identical with those examined by Lagorio (Schalféeff, Abstr., 1885, 566). J. J. S.

Reduced Acid Hæmatin. S. A. MILROY (*Proc. Physiol. Soc.*, 1904—1905, xii—xiv; *J. Physiol.*, 32).—Reduced acid hæmatin may be obtained by the use of feeble reducing agents in the cold. If a small amount of zinc dust is added to a solution of hæmatin in glacial acetic acid, the lower layer becomes bright red, but on shaking it with air it again becomes brown. But zinc dust thus used is too powerful, and some hæmatoporphyrin is formed. Better results are obtained by using a solution of hæmatin in alcohol containing 0.4 to 0.8 per cent. of oxalic acid; a trace of zinc dust is added, and reduction occurs slowly, air having first been displaced by a current of hydrogen. The red solution so formed shows a single absorption band between D and E. If a current of carbon monoxide is used instead of hydrogen, a compound is formed with two bands. A similar compound with nitric oxide was also obtained.

W. D. H.

Catalases. HANS EULER (*Arkiv Kem. Min. Geol.*, 1904, 1, 357—364).—By Senter's method (Abstr., 1903, ii, 661), pure catalase was prepared from blood, and its action is compared with that of fat catalases. Fat catalase is much less sensitive to the action of acids and bases; their influence is dependent on their concentrations.

W. D. H.

Action of Sulphuryl Chloride on Mixed Organo-magnesium Compounds. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 169—174).—The action of sulphuryl chloride on magnesium phenyl bromide mainly proceeds in two stages, in the first of which the chloride of benzenesulphonic acid is formed: (1) $\text{SO}_2\text{Cl}_2 + \text{MgBrPh} = \text{MgBrCl} + \text{SO}_2\text{PhCl}$; (2) $\text{SO}_2\text{PhCl} + \text{MgBrPh} = \text{PhCl} + \text{O}:\text{SPh}:\text{OMgBr}$. The last compound, when treated with water, yields benzenesulphonic acid.

There are also formed small amounts of chlorobenzene and diphenyl, the latter resulting from a secondary reaction: $\text{MgBrPh} + \text{C}_6\text{H}_5\text{Br} = \text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5 + \text{MgBr}_2$. This secondary reaction increases in amount as the complexity of the alkyl group in the organo-magnesium compound increases.

T. H. P.

Organic Chemistry.

General Methods of Hydrogenation and Decomposition based on the Use of Finely-divided Metals. Part II. Molecular Decompositions and Condensations. PAUL SABATIER and JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1905, [viii], 4, 433—488).—This is a general discussion of the mechanism of the action of metals in a finely-divided condition on various classes of organic compounds, in which the results recorded in the following abstracts are used as illustrations: Abstr., 1897, i, 305, 545; 1899, i, 555; 1900, i, 197, 421, 470, 471, 534; 1901, i, 195, 263, 459, 638; 1902, i, 525, 581, 701; 1903, i, 393, 453, 454, 686, 733; 1904, i, 156, 277, 303, 305, 660, and this vol., i, 254, 267. It is shown that the reactions, other than direct hydrogenation, which go on in these cases are due either to the initial formation of unstable metallic hydrides or to the combination of the metals with the organic substances employed or their decomposition products.

It is pointed out that the action of gaseous hydrogen in presence of finely-divided nickel, maintained at 250°, is capable of general application for the reduction of volatile substances, and that the passage of the vapours of primary and secondary alcohols over heated finely-divided copper is a convenient method of preparing the corresponding aldehydes and ketones.

T. A. H.

Employment of Metalammonium Compounds in Organic Chemistry; Preparation of Fatty Hydrocarbons. PAUL LEBEAU (*Compt. rend.*, 1905, 140, 1042—1044).—When the halogen substitution products of the fatty hydrocarbons are brought into contact with the blue solution of sodammonium obtained by passing perfectly dry ammonia into a tube containing sodium cooled by means of solid carbon dioxide and acetone, the corresponding hydrocarbons are obtained. When a current of methyl chloride vapour is passed into the solution, the blue colour gradually disappears and methane is evolved. Ethyl iodide and propyl iodide, when allowed to drop slowly into the solution, give rise to ethane and propane respectively. Calcium ammonium reacts in the same manner as sodammonium. If the substances employed are not perfectly dry, hydrogen is evolved. The change cannot be attributed to the action of the alkali (or alkaline earth) metal, for the products are quite different from those obtained by the reactions of Wurtz or Frankland. Polysubstituted halogen derivatives of both fatty and aromatic hydrocarbons are found to react similarly.

H. M. D.

Liquefaction of Allene and Allylene. ROBERT LESPIEAU and G. CHAVANNE (*Compt. rend.*, 1905, 140, 1035—1036).—Allene, $\text{CH}_2:\text{C}:\text{CH}_2$, prepared by the action of powdered zinc on α -epidibromohydrin in presence of alcohol and purified by repeated washing with

water and drying over calcium chloride and fused potassium hydroxide, was solidified and distilled in a vacuum. The first portion of the distillate thus obtained was used for the investigation. It melts at -146° , and its vapour pressure at this temperature is 10 mm. It boils at -32° under 760 mm. pressure; its critical temperature is 120.75° .

Allylene, $\text{CH}_2\text{C}=\text{CH}_2$, obtained from propylene bromide by the action of alcoholic sodium hydroxide, was purified in a similar manner. It melts at -110° , at which temperature its vapour pressure = 10 mm.; it boils at -23.5° under 760 mm., and its critical temperature is 129.5° .

H. M. D.

Chlorination of *n*-Propyl Alcohol. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1905, 35, i, 46—54).—The chlorination of *n*-propyl alcohol does not, as has been stated by Brochet (*Abstr.*, 1896, i, 114), give rise only to $\alpha\beta$ -dichloropropyl ether. The authors obtain a small quantity of this compound boiling at 97 — 100° under 15 mm. pressure and at 165 — 170° under the ordinary pressure, and find that on decomposition with sulphuric acid it yields β -chloropropaldehyde, which does not, however, undergo polymerisation (compare Brochet, *loc. cit.*).

From the fractions of the products of the reaction boiling either below or above 165 — 170° no definite compound could be obtained. The fraction boiling at 165 — 170° consists largely of a dichloropropyl ether, the pyridine compound of which yields, with platinic chloride, the derivative $(\text{C}_6\text{H}_{12}\text{OCl}_2, \text{C}_5\text{H}_5\text{N})_2, \text{PtCl}_4$.

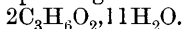
Brochet's interpretation of the mechanism of Wurtz and Frapolli's method for preparing chloroethyl ether by saturating a mixture of acetaldehyde and ethyl alcohol with hydrogen chloride (*Compt. rend.*, 1858, 47, 418) is erroneous.

T. H. P.

Normal C_6 Secondary Alcohols. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1905, 7, 19—22).—The author is engaged in investigating the influence on volatility of the displacement of various groups in these alcohols, which he proposes to synthesise by means of the action of alkyl magnesium haloids on appropriate aliphatic aldehydes.

T. A. H.

Hydrates of Acetol [Acetylcarbinol]. ANDRÉ KLING (*Compt. rend.*, 1905, 140, 1040—1042).—Comparative measurements of the viscosity of mixtures of freshly distilled acetol and water have been made. When the dependence of the viscosity on the composition is represented graphically, a curve is obtained which exhibits a series of singular points. Well pronounced maximum points correspond with the hydrates $\text{C}_3\text{H}_6\text{O}_2, \text{H}_2\text{O}$ and $\text{C}_3\text{H}_6\text{O}_2, 2\text{H}_2\text{O}$. Singular points are also found at compositions corresponding with $\text{C}_3\text{H}_6\text{O}_2, 4\text{H}_2\text{O}$ and



The viscosity of acetol which has been kept for some time is greater than that of the freshly distilled product. The viscosity curves obtained for mixtures of this modified acetol with water are analogous but not identical with those furnished by the recently distilled substance. It is supposed that the change which takes place in the

acetol is one of condensation, for on distillation of a specimen which has been kept for a time a residue of higher boiling point is obtained (compare Abstr., 1903, i, 223). H. M. D.

Normal Diprimary Glycols. I. Tetramethylene Glycol. JULES HAMONET (*Bull. Soc. chim.*, 1905, [iii], 33, 513—525).—Most of the work recorded has been published already (Abstr., 1901, i, 187, 247, 251, and 305). Tetramethylene glycol may be readily characterised by means of its *phenylurethane*, which crystallises from boiling chloroform and melts at 180—181°. T. A. H.

Synthesis of Diprimary Substances, Higher Homologues of Trimethylene Derivatives, Ethers, Dihalogenated Derivatives, Glycols, &c., by the Action of Bromomethyl Ethers of Magnesium Derivatives of Bromo- (or Iodo-) Ethers of the Type $\text{RO}(\text{CH}_2)_n\text{MgBr}$. JULES HAMONET (*Bull. Soc. chim.*, 1905, [iii], 33, 525—528).—A *résumé* of work already published (Abstr., 1904, i, 401 and 467). T. A. H.

Syntheses in the Pentamethylene Series. JULES HAMONET (*Bull. Soc. chim.*, 1905, [iii], 33, 528—533).—A *résumé* of work already published (Abstr., 1904, i, 643 and 705). T. A. H.

Hexamethylene Glycol and its Derivatives. JULES HAMONET (*Bull. Soc. chim.*, 1905, [iii], 33, 533—541).—A *résumé* of work already published (Abstr., 1903, i, 251 and 306). T. A. H.

Oxidation of Octoglycol *iso*Butyrate. KARL LESCH and ANTON MICHEL (*Monatsh.*, 1905, 26, 429—444. Compare Brauchbar and Kohn, Abstr., 1898, i, 353; Lederer, Abstr., 1901, i, 669; Kirchbaum, Abstr., 1904, i, 473).—The oxidation of octoglycol *isobutyrate* by potassium permanganate in sulphuric acid solution leads to the formation of three products depending on the concentration of the reaction mixture:

(a) A substance, $\text{C}_{11}\text{H}_{20}\text{O}_2$, which is a colourless oil, boils at 92° under 10 mm. pressure, forms an *additive* compound with 1 mol. of bromine in chloroform solution, and on hydrolysis yields *isobutyric* acid.

(b) A colourless, viscid oil, $\text{C}_{12}\text{H}_{22}\text{O}_4$, which distils at 170° under 17 mm. pressure and on hydrolysis yields *isobutyric* acid and the hydroxy-acid, $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$.

(c) An acid, $\text{C}_{12}\text{H}_{22}\text{O}_5$, which forms compact, white crystals, melts at 79°, boils at 152° under 10 mm. pressure, and is probably identical with Brauchbar and Kohn's product boiling at 156—160°. These authors' supposed keto-ester boiling at 135° under 17 mm. pressure was probably unchanged octoglycol *isobutyrate*.

On hydrolysis with aqueous potassium hydroxide, the acid, $\text{C}_{12}\text{H}_{22}\text{O}_5$, yields *isobutyric* acid and a *lactone*, $\text{C}_8\text{H}_{14}\text{O}_3$, which crystallises in stellate aggregates, melts at 66—67°, sublimes when heated above its melting point, and forms a *calcium* salt, $\text{C}_8\text{H}_{14}\text{O}_4\text{Ca}$. The constitutions of the acid $\text{C}_{12}\text{H}_{22}\text{O}_5$ and of its product of hydrolysis are discussed.

G. Y.

Esterification of Glycerol. MARCEL P. S. GUÉDRAS (*Compt. rend.*, 1905, **140**, 1034).—The formation of glycerol monoacetin from glycerol and acetic acid takes place very rapidly at the ordinary temperature if casein is present. The casein appears to be unaltered by the change and seems to act as a catalytic agent. H. M. D.

The Oxidising Action of Impure Ether. HUGO DITZ (*Ber.*, 1905, **38**, 1409—1410. Compare Rossolimo, this vol., i, 295).—The author has previously pointed out (*Abstr.*, 1901, ii, 222) that the blue solution of cobalt oxide in concentrated potassium hydroxide is only decolorised by ether when this contains peroxides. As this decolorisation by ether is quicker than that caused by hydrogen peroxide, it is inferred that the peroxides present in ether are more active than aqueous hydrogen peroxide. E. F. A.

Salts of Alkylsulphurous and Alkylsulphonic Acids. ARTHUR ROSENHEIM and WILLFRIED SAROW (*Ber.*, 1905, **38**, 1298—1305. Compare *Abstr.*, 1898, i, 290).—Molecular weight determinations by the boiling point method show methyl, ethyl, and propyl sulphites to be unimolecular. *Propyl sulphite*, $\text{SO}(\text{OPr}^a)_2$, formed by the action of thionyl chloride on propyl alcohol, is a colourless liquid with an aromatic odour, which boils at 194° . When shaken intermittently for six months with 20 per cent. aqueous potassium hydroxide, ethyl sulphite is hydrolysed to an extent of only 80 per cent., yielding potassium sulphate and potassium ethanesulphonate. Under the same conditions, ethyl ethanesulphonate is completely hydrolysed in six hours to potassium ethanesulphonate.

Sodium propyl sulphite, $\text{C}_3\text{H}_7\text{O}_3\text{SNa}$, formed by the action of sulphur dioxide on a solution of sodium propoxide, crystallises in white leaflets and loses sulphur dioxide on exposure to the air. Similar unstable, crystalline salts are formed by the action of sulphur dioxide on organic bases in absolute alcoholic solution.

The action of methyl or ethyl sulphate on alkali alkyl sulphites suspended in absolute alcohol leads to the formation of the alkali sulphate, sulphur dioxide, and traces of the alkali alkylsulphonate. When heated with ethyl iodide in absolute alcohol at 120° , sodium ethyl sulphite yields Strecker's double salt of sodium ethanesulphonate, $(\text{EtSO}_2\cdot\text{ONa})_4\text{NaI}$ (*Annalen*, 1867, **148**, 190), which is formed also by the action of sodium iodide on ethyl ethanesulphonate in a sealed tube at 150° . The corresponding potassium double salt, $(\text{EtSO}_2\cdot\text{OK})_4\text{KI}$, is formed by the action of potassium iodide on sodium ethyl sulphite, suspended in absolute alcohol, at 150 — 160° , or on ethyl ethanesulphonate at the laboratory temperature, or on ethyl sulphite at 150° . The double salt, $(\text{EtSO}_2\cdot\text{OK})_4\text{KBr}$, is formed by shaking ethyl sulphite or ethyl ethanesulphonate with potassium bromide in absolute alcoholic solution. Strecker's double salt, $(\text{EtSO}_2\cdot\text{ONa})_4\text{NaCNS}$ (*loc. cit.*), is formed similarly by the action of sodium thiocyanate on sodium ethyl sulphite. G. Y.

[**Chloroacetic Acids.**] JOHAN F. A. POOL (*Chem. Centr.*, 1905, i, 1005—1006. See this vol., ii, 425).

Chlorination of Fatty Acids. HUGO BLANK (D.R.-P. 157816).—When sulphuryl chloride is added to a warmed mixture of a fatty acid with its chloride or anhydride, chlorination takes place readily, and is complete below the boiling point of the sulphuryl chloride, hydrogen chloride and sulphur dioxide being steadily evolved. The yield of monochloro-acid is quantitative, no secondary reactions taking place.

C. H. D.

Formation of Fatty Acids from Lactic Acid when Fused with Alkali Hydroxides. HENRY S. RAPER (*J. Physiol.*, 1905, 32, 216—220).—When calcium lactate is fused with soda lime or potassium hydroxide and magnesium, a series of acids of the acetic series is formed (Hoppe-Seyler). In the present research, formic, acetic, propionic, butyric, and isobutyric acids were found; whether normal hexoic acid is also formed is doubtful. The non-volatile acids of high molecular weight are not higher fatty acids as stated by Hoppe-Seyler; they are heavier than water, are in part unsaturated, whilst their molecular weight is not far removed from that of hexoic acid. As isobutyric acid was found, Hoppe-Seyler's statement that the acids are normal is also incorrect. This mode of decomposition of lactic acid, moreover, does not explain the formation of fat from carbohydrates in the body.

W. D. H.

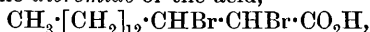
Use of Light Petroleum and Alcohol for the Separation of Oleic Acid from Stearic and other Solid Fatty Acids. K. W. CHARITSCHKOFF (*Chem. Rev. Fett. Harz. Ind.*, 1905, 12, 106—109).—From the experiments described it is seen that by treating the mixed fatty acids of a fat or oil with light petroleum of sp. gr. 0.672 or alcohol of sp. gr. 0.886 at a temperature of 0°, the oleic acid is almost completely separated from the solid fatty acids. The fraction containing the latter had a melting point of 57° and iodine value of 43.3. The solubility of stearic acid was found to be 0.4 per cent. in light petroleum and 0.1 per cent. in alcohol. Alcohol separated the oleic acid more completely than the light petroleum, but the colouring substances were insoluble and remained in the stearic acid fraction. It is preferable, therefore, especially on a manufacturing scale, firstly to separate the oleic acid by means of alcohol, and then to remove the colouring substances from the stearic acid by treating the latter with a little light petroleum.

W. P. S.

New Acids of the Oleic Series. II. Δ^a -Hypogæic Acid. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1904—1905, 40, 263—266. Compare Abstr., 1904, i, 548).—*a*-Iodopalmitic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{13} \cdot \text{CHI} \cdot \text{CO}_2\text{H}$, prepared by the action of potassium iodide on *a*-bromopalmitic acid in alcoholic solution, crystallises from light petroleum in shining plates, melts at 57°, is readily soluble in alcohol or chloroform, and remains unchanged under the influence of light.

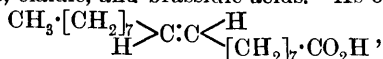
Δ^a -Hypogæic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{12} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$, obtained, together with a little *a*-hydroxypalmitic acid, by the action of alcoholic potass-

ium hydroxide solution on α -iodopalmitic acid, separates from alcohol in large, shining plates melting at 49° and resolidifying at 45° ; it is stable in the air and is soluble in light petroleum and readily so in ether or chloroform. The *sodium* salt, $C_{16}H_{29}O_2Na$, is soluble in water and crystallises from alcohol in white prisms; the *calcium* salt (with $3H_2O$) dissolves to a slight extent in alcohol, but is insoluble in water; the *barium* salt is insoluble in water or alcohol. The *amide* crystallises from alcohol in prisms and is soluble in light petroleum, ether, or chloroform. The *dibromide* of the acid,

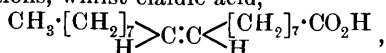


crystallises from light petroleum in white prisms melting at 66° and is soluble in the ordinary organic solvents.

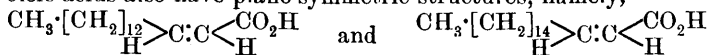
Neither Δ^{α} -hypogaëic acid nor Δ^{α} -oleic acid (*loc. cit.*), when gently heated with dilute nitric acid and treated with sodium nitrite, undergoes change, whilst the hypogaëic, oleic, and erucic acids, occurring in the vegetable kingdom, are transformed by this treatment into their isomerides, gaidic, elaidic, and brassidic acids. As oleic acid,



and erucic acid, $CH_3 \cdot [CH_2]_7 \cdot \underset{H}{\text{C}} > C : C < \underset{[CH_2]_{11} \cdot CO_2H}{H}$, have centro-symmetric configurations, whilst elaidic acid,



and brassidic acid, $CH_3 \cdot [CH_2]_7 \cdot \underset{H}{\text{C}} > C : C < \underset{H}{[CH_2]_{11} \cdot CO_2H}$, have plano-symmetric configurations, it may be assumed that Δ^{α} -hypogaëic and Δ^{α} -oleic acids also have plano-symmetric structures, namely,



respectively, which is in agreement with their relatively high melting points.

T. H. P.

Tetra-carbon Hydroxy-acids obtained by the Action of Hydrogen Cyanide on Epichlorohydrin, Epibromohydrin, and Epiethylin (Ethyl Glycide Ether). ROBERT LESPIEAU (*Bull. Soc. chim.*, 1905, [iii], 33, 460—469).—Most of the results recorded have already been published (Abstr., 1899, i, 243, 790; 1900, i, 425; 1903, i, 547, 684; 1904, i, 286, 471, and this vol., i, 9 and 255). When α -cyano- β -hydroxy- γ -ethoxypropane (this vol., i, 255) is treated with phosphoric oxide it yields γ -ethoxycrotononitrile, $OEt \cdot CH_2 \cdot CH : CH \cdot CN$, which is liquid, boils at 190 — 191° under 750 mm. and at 82.5° under 17 mm. pressure. Ethyl γ -ethoxycrotonate, obtained by dehydrating ethyl β -hydroxy- γ -ethoxybutyrate (*ibid.*), boils at 201 — 203° under 760 mm. and at 95 — 96° under 19 mm. pressure and on hydrolysis with potassium hydroxide furnishes the corresponding acid. The latter is crystalline, melts at 45° , boils at 145 — 146° under 26 mm. pressure, and on oxidation with barium permanganate yields ethyl-erythric acid, $OEt \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CO_2H$, which crystallises from benzene, melts at 90 — 92° , and yields a gummy calcium salt.

T. A. H.

Semialdehyde of Maleic Acid. HERMANN FECHT (*Ber.*, 1905, 38, 1272—1274. Compare Limpricht, this Journal, 1873, 624; Baeyer, *Ber.*, 1877, 10, 1362; Hill and Allen, *Abstr.*, 1897, i, 556).—An aqueous solution of bromine ($3\frac{1}{3}$ mols.) and potassium hydroxide (4 mols.) is added to a suspension of pyromucic acid (1 mol.) in water at 0°, the mixture, after remaining a day at the ordinary temperature, warmed to 30°, saturated with sodium sulphate, and extracted with ether, and the residue, obtained by evaporating the dry extract in a vacuum, distilled from the water-bath under 0.1—0.3 mm. pressure. The semialdehyde of maleic acid, $C_4H_4O_3$, obtained in this manner, crystallises from a mixture of benzene and ether in flat needles, melts at 55°, and boils with slight decomposition at 145° under 10 mm. pressure; in a thick layer, in concentrated aqueous or ethereal solution, or when fused, it is yellowish-green; it is easily soluble in water, alcohol, or ether, reduces ammoniacal silver or Fehling's solution, and colours rosaniline in sulphurous acid solution.

The *phenylhydrazone*, $C_{10}H_{10}O_2N_2$, crystallises in lemon-coloured needles and melts at 158—159°. The *oxime*, $C_4H_5O_3N$, forms a white, crystalline crust and detonates at 130—140°. The action of hydrogen chloride on the oxime in methyl-alcoholic solution leads to the formation of dimethyl fumarate.

When neutralised with sodium hydrogen carbonate and warmed with potassium cyanide in aqueous solution, maleic acid semialdehyde yields succinic acid. G. Y.

Formation of Salts in Solution, especially in the case of Substances exhibiting Tautomerism (Pseudo-acids, Pseudo-bases). III. JULIUS W. BRÜHL and HEINRICH SCHRÖDER (*Zeit. physikal. Chem.*, 1905, 51, 513—541. Compare *Abstr.*, 1904, i, 646, 969; this vol., ii, 70, 235).—A rehearsal in the first place of the evidence in favour of the view that the esters of acetoacetic acid, their monoalkyl derivatives, and the esters of camphorcarboxylic acid are pure ketonic substances, without any traces of the enolic forms. Comparison of the spectrochemical functions shows that these substances are strictly homologous with the dialkyl derivatives of the esters of acetoacetic acid and the alkyl derivatives of the esters of camphorcarboxylic acid respectively. The latter compounds are undoubtedly ketonic, hence the former must also be ketonic. Further, the spectrochemical function for ethyl acetoacetate dissolved in water, methyl alcohol, or chloroform has the same value as for the pure ester, and a similar remark applies to methyl camphorcarboxylate dissolved in methyl alcohol or chloroform. Hence the forms in which the esters are present in these media are undoubtedly ketonic. The marked change of spectrochemical function when the esters are dissolved in a salt-forming medium, such as an alcoholic solution of sodium ethoxide, indicates that in these circumstances enolisation takes place immediately and can be easily detected.

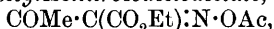
These conclusions are not in harmony with some of Brühl's observations on the ferric chloride reaction (see *Abstr.*, 1903, i, 314). The view is now adopted that ferric chloride is not a trustworthy reagent for the distinction of ketonic and enolic forms. As a salt, it is some-

what analogous to sodium ethoxide, and it may, like the latter, first induce enolisation when the medium permits, and only then give the characteristic reaction.

The paper contains a supplementary note, in which Brühl criticises Dimroth's recent work (this vol., i, 98) and emphasises the general applicability and trustworthiness of the optical method in settling problems of desmotropy. J. C. P.

Action of Hydroxylamine on Ethyl *iso*Nitrosoacetoacetate. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 1431).—A reply to Bouveault and Wahl (this vol., i, 257). J. J. S.

Ethyl Acetylisonitrosoacetoacetate. ANDRÉ WAHL (*Bull. Soc. Chim.*, 1905, [iii], **33**, 486—490).—In the preparation of ethyl diketobutyrate by the method already described (*Abstr.*, 1904, i, 556, and next page), *ethyl acetylisonitrosoacetoacetate*,

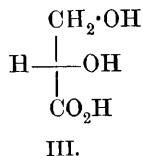
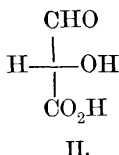
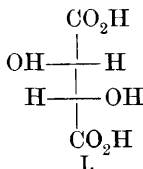


is formed; this substance may also be obtained by the action of acetic anhydride on ethyl *isonitrosoacetoacetate*. It is a viscid, slightly yellow liquid, which boils at 145° under 20 mm. pressure, and is heavier than, and insoluble in, water. Alkalis decompose it, forming a mixture of the cyanide, acetate, and carbonate of the alkali used. With hydroxylamine hydrochloride, ethyl dioximinobutyrate is produced. Phenylhydrazine reacts with ethyl acetylisonitrosoacetoacetate to form acetylphenylhydrazine and *ethyl α -acetylloximino- β -phenylhydrazinobutyrate*, $\text{NHPh}\cdot\text{N}\cdot\text{COMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{OAc}$, which crystallises in yellow needles and melts at 123—124° and on treatment with potassium hydroxide in alcohol furnishes *ethyl α -oximino- β -phenylhydrazinobutyrate*, crystallising from alcohol in colourless spangles and melting at 165—166° when projected on the mercury bath. This ester may also be prepared by the action of phenylhydrazine on ethyl *isonitrosoacetoacetate* dissolved in acetic acid, but in this case there is also formed Knorr's *isonitrosophenylmethylpyrazolone*, due to loss of a molecule of ethyl alcohol (*Abstr.*, 1887, 602). T. A. H.

Formation of Lævulic Acid and of Alcohol from Sugars. EMIL ERLÉNMEYER, jun. (*J. pr. Chem.*, 1905, [ii], **71**, 382—384).—Suggestions are made as to the intermediate substances formed in the production of lævulic acid by the action of hydrochloric acid on dextrose or lævulose, and of alcohol by fermentation. G. Y.

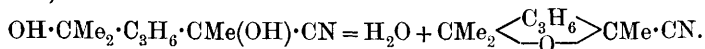
Glyceric Acid Derivatives. III. Configuration of Glyceric Acid. CARL NEUBERG and MARTIN SILBERMANN (*Zeit. physiol. Chem.*, 1905, **44**, 134—146. Compare *Abstr.*, 1904, i, 220).—Details of the preparation of Will's hydroxypyruvic acid (aldehydoglyceric acid), $\text{CHO}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ (*Abstr.*, 1891, 542), from nitrocellulose are given. As solutions of the salts are lævorotatory, it cannot have the ketonic constitution suggested by Will. The most characteristic derivative is the *brucine* salt, $\text{C}_{29}\text{H}_{26}\text{O}_4\text{N}_2\cdot\text{C}_3\text{H}_4\text{O}_3$, which crystallises from water in colourless needles. The acid readily reacts with potassium cyanide,

yielding a hydroxy-nitrile, which on hydrolysis yields *L*-tartaric acid. As the configuration of *l*-tartaric acid, I, is known to be



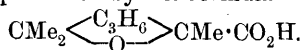
the configuration II must necessarily represent that of the aldehydglyceric acid molecule, and as this on reduction yields *l*-glyceric acid, configuration III must represent *l*-glyceric acid. The transformation of cellulose (a derivative of dextrose) into *l*-glyceric acid derivatives is analogous to the transformation of *d*-glycuronic acid into *l*-xylose (Abstr., 1903, i, 7), and of *d*-galactose into *l*-sorbosose (Abstr., 1900, i, 208, 332). J. J. S.

Cineolic Acid. IV. Synthesis and Constitution of Cinenic Acid. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1905, 38, 1502—1507. Compare Abstr., 1900, i, 371; 1901, i, 119, 578).— β -Hydroxy- β -methyl- ζ -heptanone, $\text{OH}\cdot\text{CMe}_2\cdot[\text{CH}_2]_3\cdot\text{CMe}$, prepared by the action of dilute sulphuric acid on methylheptenone, boils at 106° under 9 mm. and at 115 — 117° under 14 mm. pressure (compare Verley, Abstr., 1898, i, 557). When heated for 24 hours at 80° with anhydrous hydrogen cyanide, it forms *cinenonitrile*, which boils at 74.5° under 9 mm. pressure, water being eliminated from the nitrile initially formed, thus:



Cinenamide, $\text{C}_9\text{H}_{17}\text{O}_2\text{N}$, prepared by the action of alcoholic potassium hydroxide on the nitrile, separates from dilute alcohol in white needles and melts at 86 — 87° . When either the nitrile or the amide is hydrolysed by concentrated aqueous sodium hydroxide, cinenic acid is formed and is identical with the product previously described by Rupe and Ronus (*loc. cit.*).

Cinenic acid is represented by the formula



A. McK.

Preparation of $\alpha\beta$ -Diketobutyric Esters. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], 33, 475—481. Compare Sachs and Wolff, Abstr., 1903, i, 792, and Wieland and Bloch, *ibid.*, 1904, i, 596).—Many of the results recorded have already been published (Abstr., 1904, i, 556). Further details regarding the methods employed and some of the substances prepared are now given. Ethyl diketobutyrate hydrate, $\text{COMe}\cdot\text{CO}\cdot\text{CO}_2\text{Et}, \frac{1}{2}\text{H}_2\text{O}$ (*loc. cit.*), melts at 140° when projected on the mercury bath; isobutyl diketobutyrate hydrate, under the same conditions, melts at 115 — 120° (*loc. cit.*). *Methyl diketobutyrate*, prepared by the general method (*loc. cit.*), is a

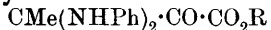
pleasant-smelling, mobile, orange-yellow liquid, which boils at 65—68° under 12 mm. pressure; the *hydrate*, $\text{COMe} \cdot \text{CO} \cdot \text{CO}_2\text{Me} \cdot \text{H}_2\text{O}$, crystallises from a mixture of ether and light petroleum and melts at 79—80°.

T. A. H.

Reactions of Diketobutyric Esters. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], 33, 481—486. Compare Abstr., 1904, i, 556 and 789, and preceding abstract).—The diketobutyric esters dissolved in acetic acid react with semicarbazide to form disemicarbazones, which are insoluble in most solvents and melt at comparatively high temperatures. *Methyl diketobutyrate disemicarbazone* melts at about 250°, and the *disemicarbazone* of the ethyl ester at about 270°.

With hydrazine in aqueous solution, the esters give rise to a *substance* which crystallises from acetic acid in ruby-red needles, melts above 300°, and dissolves in alkalis with an intensely violet colour. It is suggested that Knorr's rubazonic acid (Abstr., 1887, 602), which behaves similarly, may be a diphenyl derivative of this substance.

The diketobutyric esters combine with 2 mols. of aniline forming dianilides, which retain persistently 1 mol. of water and are therefore probably represented by one of the two formulæ



or $\text{COMe} \cdot \text{C}(\text{NHPh})_2 \cdot \text{CO}_2\text{R}$. When these compounds are treated with phenylhydrazine, they are converted into phenylhydrazinophenylmethylpyrazolones.

Ethyl diketobutyrate dianilide, $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$, crystallises from alcohol in colourless needles and melts at 117—118°; the corresponding *derivatives* of the methyl and isobutyl esters are similar and melt at 115° and 114° respectively.

isoButyl diketobutyrate phenylhydrazone crystallises from a mixture of benzene and light petroleum in yellow, rhomboidal tablets and melts at 98°; the *phenylhydrazone* of the methyl ester is similar and melts at 98—99°. When boiled in acetic acid solution, both these phenylhydrazones yield Knorr's rubazonic acid (Abstr., 1887, 602), which indicates that they are β -phenylhydrazones (compare Abstr., 1904, i, 789).

T. A. H.

Constitution of Certain Organic Salts of Nickel and Cobalt as they exist in Aqueous Solution. OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1905, 27, 386—391. Compare Abstr., 1903, ii, 134).—The investigations described in the earlier paper have been extended to the determination of the conductivity and freezing points of the nickel, cobalt, and magnesium glutarates, α -hydroxyglutarates, and trihydroxyglutarates.

It is found that the conductivity of these cobalt and nickel salts is somewhat greater than that of the corresponding malates and tartrates, but that the conductivity decreases as the number of hydroxyl groups increases, just as in the case of the succinic acid series.

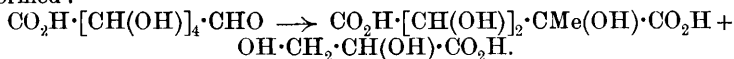
These salts show but little tendency to polymerise, but the amount of polymerisation increases with the number of hydroxyl groups in the molecule. The tendency to undergo polymerisation shown by the cobalt and nickel malates and tartrates, however, does not appear to

increase in the case of the salts of the higher hydroxy-acids of this series. E. G.

α -Chloroglutaconaldehyde [β -Chloropenta- $\Delta^{\alpha\gamma}$ -dien- α -ol- ϵ -al]. WALTER DIECKMANN (*Ber.*, 1905, 38, 1650—1654. Compare Abstr., 1902, i, 786).—The author regards the compound described by Hantzsch as 3-chloro-1:2-diketocyclopentane (Abstr., 1889, 853) as the α -chloro-derivative of glutaconaldehyde, which has not been obtained in the free state, but which is the parent compound of the glutaconaldehyde dianilide obtained by Zincke (Abstr., 1904, i, 448 and 921; 1905, i, 241) and by Koenig (Abstr., 1904, i, 449). If this is so, the compound described by Ince (Abstr., 1890, 1090) as the dianilide of chlorodiketocyclopentane, being really a chloro-derivative of the glutaconaldehyde dianilide, must exhibit close analogy in properties with the latter. This is in reality the case, for Ince's dianilide exhibits in its salts the same tinctorial characteristics as are shown by Zincke and Koenig's dianilide. Further, the former is formed from 3-chloropyridine (by means of cyanogen bromide and aniline) and the latter from pyridine, and when boiled with hydrochloric acid the former is resolved into aniline and 3-chloro-1-phenylpyridinium chloride, which is perfectly analogous with phenylpyridinium chloride obtained in a similar way from Zincke and Koenig's dianilide.

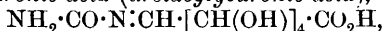
3-Chloro-1-phenylpyridinium chloride, $\text{CH} \begin{smallmatrix} \text{CCl}:\text{CH} \\ \text{CH}-\text{CH} \end{smallmatrix} \text{NPhCl}$, is readily soluble in water or alcohol, and forms colourless crystals; the *platinichloride*, $(\text{C}_{11}\text{H}_9\text{NCl}_2)_2\text{PtCl}_4$, crystallises from water in orange-red needles, melting and decomposing at 200—203°. T. H. P.

New Reactions and Derivatives of Glycuronic Acid. VII. CARL NEUBERG and WILHELM NEIMANN (*Zeit. physiol. Chem.*, 1905, 44, 97—113).—The action of calcium hydroxide solution on glycuronic acid is similar to its action on dextrose (Kiliani, *Ber.*, 1882, 15, 701 and 2957). When a 14 per cent. solution of glycuronic acid is left in contact with calcium hydroxide for several months, oxygen is absorbed and saccharone (Kiliani, Abstr., 1883, 962) and *l*-glyceric acid are formed:



Free glycuronic acid and solutions of its lactone do not react with hydrogen cyanide, even in the presence of a small amount of ammonia, but potassium cyanide and glycuronic acid react, forming a nitrile which, on hydrolysis, yields α -pentahydroxypimelic acid (Kiliani, Abstr., 1886, 936). Although the formation of two stereoisomeric acids is possible, only one has been isolated in the form of its calcium salt.

Carbamidoglycuronic acid (ureidoglycuronic acid),



is formed when a solution of glycuronic anhydride and carbamide in 5 per cent. sulphuric acid is kept for $2\frac{1}{2}$ months at 40°. It is most readily isolated as the *barium* salt, $\text{C}_{14}\text{H}_{22}\text{O}_{14}\text{N}_4\text{Ba}$, which dissolves in

water, but is precipitated on the addition of absolute alcohol. The salt does not reduce, but when boiled for some time with Fehling's solution a precipitate of cuprous oxide is suddenly produced. It is laevorotatory, like all condensed glycuronic acid, and has $[\alpha]_D - 15.83^\circ$ at 17° . It is not hydrolysed by enzymes, such as kephir lactase, emulsin, or maltase. The free acid has only been obtained in aqueous solution. When this solution is concentrated, the acid is hydrolysed into its components. The addition of salts of heavy metals to solutions of the barium salt produces no precipitate.

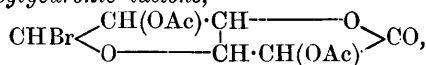
Glycuronic acid osazone, $\text{CO}_2\text{H} \cdot [\text{CH}(\text{OH})]_3 \cdot \text{C}(\text{N}_2\text{HPh}) \cdot \text{CH} : \text{N}_2\text{HPh}$, may readily be obtained pure by Wohl and Neuberg's method (*Ber.*; 1900, 33, 3108), using a temperature of 40° . It crystallises from 50 per cent. alcohol in long, felted needles, melts at $200-202^\circ$, and in most respects closely resembles glucosazone. It possesses acidic properties, and yields precipitates with baryta water or barium acetate solution.

The *osazone hydrazide*,

$\text{NHPh} \cdot \text{NH} \cdot \text{CO} \cdot [\text{CH}(\text{OH})]_3 \cdot \text{C}(\text{N}_2\text{HPh}) \cdot \text{CH} : \text{N}_2\text{HPh}$, is obtained when an alcoholic solution of the osazone is heated with phenylhydrazine at 150° . It crystallises in yellow, felted needles, changes colour at 210° , melts and decomposes at 212° , and is less readily soluble than the osazone. J. J. S.

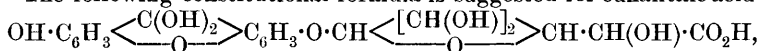
Synthesis of Condensed Glycuronic Acids. VIII. CARL NEUBERG and WILHELM NEIMANN (*Zeit. physiol. Chem.*, 1905, 44, 114—126).—The natural condensed glycuronic acids are usually represented as being closely related to the glucosides. Such constitutional formulæ have been confirmed by the synthesis of phenolglycuronic acid, euxanthic and isoeuxanthic acids.

Diacetylbromoglycuronic lactone,



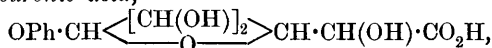
obtained by the action of acetyl bromide on glycuronolactone, crystallises in colourless needles, melts at 90° (corr.), dissolves readily in alcohol, ether, or ethyl acetate, is rapidly decomposed by water, and does not reduce cold Fehling's solution. When condensed with potassium methoxide and euxanthone in methyl-alcoholic solution, it yields an acid identical with natural euxanthic acid and an isomeric acid, *isoeuxanthic acid*, $\text{C}_{19}\text{H}_{16}\text{O}_{10}$, which melts at $157-159^\circ$. Its rotatory power is less than that of euxanthic acid, $[\alpha]_D - 87.4^\circ$.

The following constitutional formula is suggested for euxanthic acid :



and a similar formula, less H_2O , for the *iso*-acid, the OH group probably occupying different positions in the two acids.

Phenolglycuronic acid,

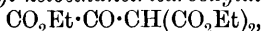


crystallises from water in long, prismatic needles when free from glycuronic acid, melts at $150-151^\circ$, has $[\alpha]_D^{17} - 83.3^\circ$, is readily soluble

in alcohol and hot ethyl acetate, and yields soluble salts. It is probably identical with the substance described by Kütz (Abstr., 1890, 1286).

J. J. S.

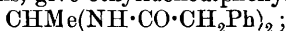
Action of Ethyl Oxalic Chloride on Ethyl Sodiomalonate. HERBERT KURREIN (*Monatsh.*, 1905, 26, 373—378).—The action of ethyl oxalic chloride on ethyl sodiomalonate in benzene solution leads to the formation of *ethyl ketoethanetricarboxylate*,



which is a colourless oil; it boils at 86° under 12 mm. pressure, and is hydrolysed by boiling alcoholic potassium hydroxide. The acid, $\text{C}_5\text{H}_4\text{O}_7 \cdot 2\text{H}_2\text{O}$, melts at 99° , loses carbon dioxide at 120 — 130° , and forms an anhydrous calcium salt, $(\text{C}_5\text{H}_4\text{O}_7)_2\text{Ca}_3$.

G. Y.

Action of Hydrogen Chloride on Mixtures of Nitriles and Aldehydes or Ketones. FRANZ HENLE and GUSTAV SCHUPP (*Ber.*, 1905, 38, 1369—1371).—When acetonitrile is mixed with either acetaldehyde, benzaldehyde, acetone, or acetophenone, and hydrogen chloride passed into the mixture, a small quantity of acetamide hydrochloride is obtained; with acetone, propionitrile gives propionamide hydrochloride under similar conditions. On passing hydrogen chloride into a mixture of benzonitrile and acetaldehyde, ethylidenedibenzamide, $\text{CHMe}(\text{NHBz})_2$, is formed; benzyl cyanide and acetaldehyde, under similar conditions, give ethylidenediphenylacetamide,



benzyl cyanide and acetone give phenylacetamide. Benzonitrile and benzyl cyanide are not changed by benzaldehyde or acetophenone in presence of hydrogen chloride.

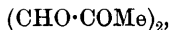
W. A. D.

Preparation of Mesoxaldialdehyde. FRANZ HENLE and GUSTAV SCHUPP (*Ber.*, 1905, 38, 1372—1373).—On passing nitrous vapours into an ice-cold aqueous suspension of diisonitrosoacetone, nitrous oxide is evolved, and a solution containing mesoxaldehyde, $\text{CO}(\text{CHO})_2$, is obtained; that about 30 per cent. of this substance is formed is shown by the production of mesoxaldialdehydebisphenylhydrazone on adding phenylhydrazine acetate and sodium acetate to the cold solution.

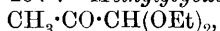
When nitrous acid is passed into a suspension of diisonitrosoacetone in ether, garnet-red crystals separate, which effloresce and become yellow in the air and explode when heated; on adding cold dilute solutions of sodium or barium hydroxide, ammonia, potassium cyanide, or sodium acetate to this substance, an explosion, accompanied by a large yellow flame, occurs. The behaviour of the substance resembles that of nitroamide.

W. A. D.

Methylglyoxal and Mesoxaldialdehyde. CARL D. HARRIES and HANS TÜRK (*Ber.*, 1905, 38, 1630—1636. Compare Abstr., 1903, i, 605).—*Mesityl oxide ozonide*, $\text{C}_6\text{H}_8\text{O}_5$, is obtained as a very explosive, viscous green syrup. When gently heated in solution, it gives acetone peroxide, $\text{CMe}_2 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$, and the di-polymeride of *methylglyoxal*,



which forms a hygroscopic, glassy mass. *Methylglyoxal semicarbazone*, $C_3H_{10}O_2N_6$, dissolves slightly in water, from which it separates in crystals melting at about 257° . *Methylglyoxal monoacetal*,



prepared by the action on methylglyoxal of absolute alcohol containing 2 per cent. of hydrogen chloride, is obtained as a highly refractive liquid boiling at 30° under 10 mm. pressure.

Phorone diozonide, $C_9H_{14}O_7$, is obtained as an explosive, pale green, viscous syrup which ignites if left in the air. It is gradually decomposed by ice-water, yielding acetone peroxide and a *hydrate* of mesoxal-dialdehyde, $C_3H_4O_4$, which is a clear, viscous syrup. Anhydrous *mesoxal-dialdehyde*, $CHO \cdot CO \cdot CHO$, forms a pale yellow, brittle mass which is extremely hygroscopic. The melting point of the triphenylhydrazone prepared by the authors is 156° , whereas von Pechmann and Jenisch gave 166° (Abstr., 1892, 161).
T. H. P.

Chemical Action of Light. IX. GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1905, **38**, 1671—1675. Compare this vol., i, 335).—A mixture of acetone and aqueous 3·3 per cent. hydrogen cyanide, exposed to sunlight for several months, gave rise to the following products: ammonium oxalate, acetonylecarbamide, α -hydroxyisobutyramide, α -aminoisobutyric acid. In the dark, the sole product formed was acetone cyanohydrin. Similarly, aldehyde-ammonia and aqueous 3·3 per cent. hydrogen cyanide, after six months' exposure to sunlight, gave rise to a yellowish-brown, gummy product, from which a *compound*, $C_6H_{12}O_3N_2$, isomeric with alanylalanine, was obtained. This crystallises in thick, colourless plates melting at 232° , and probably has the constitution $CO_2H \cdot CHMe \cdot NH \cdot CHMe \cdot CO \cdot NH_2$.

E. F. A.

Methylheptenone Oxides. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1905, **38**, 1498—1502).—Methylheptenol, prepared by the reduction of methylheptenone by sodium, boils at 74 — 75° under 10 mm. pressure. When agitated for 16—20 hours with dilute sulphuric acid, it is converted into the glycol, β -methylheptane- $\beta\zeta$ -diol, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot OH$, a viscid oil, which boils at 122 — 123° under 13 mm. pressure and, when distilled with sulphuric acid in a current of steam, gives cinene, boiling at 127 — 128° (Wallach gives 127 — 129°). Cinene yields white needles or prisms of an *additive compound* with hydrogen bromide in acetic acid solution, which is stable only in presence of an excess of hydrogen bromide and undergoes immediate decomposition in air.

Dimethylheptenol, prepared by the action of magnesium methyl iodide on methylheptenone, boils at 76 — 78° under 12 mm. pressure (Barbier gives 79° under 12 mm. pressure). By the action of sulphuric acid, it is converted into the glycol, $\beta\zeta$ -dimethylheptane- $\beta\zeta$ -diol, $OH \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$, which separates from ether in glassy crystals and melts at 62° ; the *diacetyl* derivative is a viscid oil, which boils at $135\cdot5$ — 136° under 14 mm. pressure. When the glycol is added to an ice-cold solution of 70 per cent. sulphuric acid, it is

dehydrated, *methylcinene*, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix} \text{O}$, being formed as an oil boiling at $142\text{--}142.5^\circ$ under 744 mm. pressure. By the action of a mixture of glacial acetic acid and hydrogen bromide, it is converted into an additive compound, $\text{C}_9\text{H}_{19}\text{OBr}$, crystallising in needles and melting at $63\text{--}64^\circ$; the latter compound is instantaneously decomposed by water. Methylcinene forms an additive compound with hydroferri-cyanic acid. A. McK.

Preparation of β -Methylglucoside. LÉON MAQUENNE (*Bull. Soc. chim.*, 1905, [iii], 33, 469—471).—Dextrose is dissolved in water and methyl sulphate is added together with enough potassium hydroxide solution of sp. gr. 1.4 to render the liquid alkaline until the end of the reaction, when it should be almost neutral. After 30 minutes, the mixture is concentrated, poured into excess of alcohol, and the filtrate evaporated to a syrup and set aside to crystallise. After recrystallisation twice from warm alcohol, a yield of β -methylglucoside equivalent to 20 per cent. of the weight of dextrose employed is obtained. A further quantity may be secured by re-treatment of the residues with methyl sulphate and potassium hydroxide. The glucoside softens at 96° and loses a $\frac{1}{2}$ mol. of water and then melts at about 108° . No α -methylglucoside is formed by this method. T. A. H.

Action of Inorganic Compounds on Optically Active Polyhydric Alcohols and Acids. HERMANN GROSSMANN (*Ber.*, 1905, 38, 1711—1719. Compare Rimbach and Weber, following abstract).—A solution of lead acetate in presence of sodium hydroxide produces a considerable increase in the molecular rotation of dextrose solutions. The increased rotation is observed immediately after mixing and it shows a tendency to fall again after a short time. Lead acetate solution itself produces but little effect; this increases with the time (Lobry de Bruyn and Alberda van Ekenstein, *Abstr.*, 1896, i, 116 and 588). The effect of an alkaline lead acetate solution on lævulose is to diminish the lævorotation and ultimately to induce dextrorotation; this reaches its maximum, $[\alpha]_D + 66.7^\circ$ at 17° , when the ratio of lævulose to lead acetate molecules is 2 : 3. If the concentration of the acetate is increased, the dextrorotation decreases and ultimately changes sign again.

A solution of invert sugar in the presence of alkaline lead acetate changes from lævo- to dextro-rotatory, reaches a maximum, and then diminishes with increasing lead acetate concentration.

Mannitol in the presence of neutral bismuth nitrate (molecular proportions) exhibits a dextrorotation which increases with dilution. No multirotation is shown on keeping, although some change goes on in the solution. In the presence of alkali, bismuth nitrate produces a still more marked effect on the rotation of mannitol.

Rosenheim and Schütte's ammonium titanotartrate (*Abstr.*, 1901, ii, 246) is lævorotatory in concentrated solution, but on dilution becomes strongly dextrorotatory. For $c = 2.317$, $[\alpha]_D$ is -40.1° , and for $c = 0.1448$ $[\alpha]_D$ is $+276.3^\circ$ at 20° . J. J. S.

Action of Inorganic Substances on the Rotation of Lævulose and Dextrose. EBERHARD RIMBACH and O. WEBER (*Zeit. physikal. Chem.*, 1905, 51, 473—493. Compare Rimbach and Schneider, *Abstr.*, 1903, ii, 624).—The chlorides of the alkaline earth metals have little effect on the rotation of dextrose, but raise the rotation of lævulose to an extent which increases with their concentration. The relative effect of zinc, cadmium, and mercury salts is similar. The influence of free boric acid on the rotation of lævulose and dextrose is practically nil, but the conductivity of the solutions containing both sugar and acid is higher than that of the solutions containing the acid alone—a contrast to the usual effect of the sugars, which is to diminish the conductivity of the inorganic substance. Borax reduces very markedly the rotation of both lævulose and dextrose. Cerium and thorium salts have a very slight effect on the rotation of dextrose, but increase that of lævulose to a notable extent. Zirconium oxychloride reduces the rotation of both sugars very markedly, the effect being greatest in the case of dextrose. The final value of the rotation, however, is reached only after some time, and the sugar solutions containing larger quantities of zirconium gradually assume an intense reddish-brown colour. When a solution of lævulose or dextrose containing zirconium salt is warmed, a green fluorescence is observed—a behaviour exhibited also by several other sugars. Arsenious acid raises slightly the rotation of lævulose, but is without effect on that of dextrose. The influence of compounds of molybdenum, tungsten, and uranium is varied and of no very definite character.

The effect of borax, referred to above, is probably due, to a certain extent at least, to the presence of hydroxyl ions produced by hydrolysis. This leads the authors to study quantitatively the action of hydroxyl ions (from sodium hydroxide, triethylamine, and sodium carbonate) on dextrose. It is found that the reaction, as followed by the change of rotation, is one of the second order. When the other conditions are fixed, the velocity is proportional to the concentration of the hydroxyl ions.

J. C. P.

Nature of Iodide of Starch. MAURICE PADOA and B. SAVARÉ (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 467—476).—The authors show, by conductivity measurements, that iodide of starch must be regarded as an additive product of iodine, starch, and potassium iodide (or hydrogen iodide), the molecular ratio between the iodine and starch ($C_6H_{10}O_5$) being 4. It was not found possible to obtain a constant relation between the iodine and hydriodic acid. The existence is proved of only one additive product, the modifications of the colour being probably caused by physical modifications of the particles of the iodide of starch. The latter forms solutions of the nature of suspensions.

T. H. P.

Preparation of Betaine Salts from Molasses. CARL STIEPEL (D.R.-P. 157173. Compare Staněk, *Abstr.*, 1902, i, 427).—In the extraction of betaine from molasses and similar products, the employment of chemical reagents to break up the complex compounds present has hitherto been considered necessary. It is now

found that the betaine may be extracted by simple agitation with 95 per cent. alcohol. The alcoholic solution is decolorised by charcoal and evaporated to a syrup. It may be again dissolved in alcohol and the betaine hydrochloride precipitated by the addition of concentrated hydrochloric acid or gaseous hydrogen chloride.

C. H. D.

Electrolysis of Glycine. OTTO KÜHLING (*Ber.*, 1905, 38, 1638—1646).—Aqueous glycine solutions are at first very bad conductors, but as the electrolysis proceeds the conductivity of the solutions increases owing to the formation of better conducting products.

After electrolysis, the solutions are found to contain ammonia and small quantities of ethylenediamine, whilst if the conductivity of the original solution is increased by the addition of an indifferent substance, no ethylenediamine is obtained. The gaseous products consist almost entirely of carbon dioxide, whilst carbon monoxide, nitrogen, and formic acid are formed in small quantities.

The resolution of glycine by electrolysis probably takes place in two ways: (1) Giving NH_3 and $\text{CH}_2\cdot\text{CO}_2'$ and (2) giving $\cdot\text{NH}_3\cdot\text{CH}_2\cdot$ and CO_2' .

T. H. P.

Ethyl Diaminosuccinate. JULIUS TAFEL and HERMANN STERN (*Ber.*, 1905, 38, 1589—1592. Compare Tafel, *Abstr.*, 1887, 468; Farchy and Tafel, *Abstr.*, 1893, i, 692).—Ethyl μ -diaminosuccinate, $\text{C}_8\text{H}_{16}\text{O}_4\text{N}_2$, obtained from its hydrochloride by Curtius' method, crystallises in long needles, melts at 38° , distils at 160 — 166° under 15 mm. pressure, has an alkaline reaction in aqueous solution, gives a blue coloration with copper sulphate, and forms a picrate melting at 121° . The diacetyl derivative, $\text{C}_{12}\text{H}_{20}\text{O}_6\text{N}_2$, crystallises in plates and melts at 180.5° ; the dibenzylidene derivative crystallises in needles, melts at 144.5° , and is hydrolysed by cold 10 per cent. hydrochloric acid; the condensation product with ethyl acetoacetate, $\text{C}_{20}\text{H}_{32}\text{O}_8\text{N}_2$, crystallises in prismatic needles and melts at 77° ; the condensation product with acetylacetone, $\text{C}_{18}\text{H}_{28}\text{O}_6\text{N}_2$, crystallises in prismatic needles and melts at 138 — 139° .

G. Y.

α -Amino-derivatives of Adipic Acid, β -Methyladipic Acid, and Pimelic Acid. WALTHER DIECKMANN (*Ber.*, 1905, 38, 1654—1661).— α -Aminoadipic acid (Sørensen, *Abstr.*, 1903, i, 833), $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, prepared by the reduction of α -hydroxyaminoadipic acid with tin and hydrochloric acid, crystallises in colourless, microscopic plates, which melt and decompose at 205 — 206° and give a reddish-brown coloration with ferric chloride; the copper salt (with $2\text{H}_2\text{O}$) separates as a deep blue, crystalline precipitate.

2-Piperidone-6-carboxylic acid, $\text{C}_5\text{NH}_8\text{O}\cdot\text{CO}_2\text{H}$, formed on heating α -aminoadipic acid at its melting point, crystallises from water in transparent, pointed prisms, melting at 177 — 178° , and forms crystalline copper, barium, and silver salts.

δ -Amino- β -methyladipic acid,



was isolated in the form of a very sparingly soluble *copper* salt crystallising with $2\text{H}_2\text{O}$. *α-Benzamino-γ-methyladipic acid* crystallises in colourless needles melting at $172\text{--}173^\circ$. *4-Methyl-2-piperidone-6-carboxylic acid*, $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \\ \text{CH}_2 \text{---} \text{CO} \end{array} \text{NH}$, crystallises in well-formed, transparent prisms melting at 124° , and forms a green, crystalline *copper* salt; the *silver* salt separates in colourless needles.

α-Aminopimelic acid, $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$, forms colourless, microscopic plates melting and decomposing at 225° ; the bright blue *copper* salt is sparingly soluble. E. F. A.

Synthesis of Aminohydroxysuccinic Acid. CARL NEUBERG and MARTIN SILBERMANN (*Zeit. physiol. Chem.*, 1905, **44**, 147—156. Compare Abstr., 1904, i, 220).—Aminohydroxy-acids may be obtained from diamino-acids by means of nitrous acid. Care must be taken that only the theoretical amount of nitrous acid is employed; this may be accomplished by using silver nitrite and the hydrobromide of the base or barium nitrite and the sulphate of the base (Witt and Ludwig, Abstr., 1904, ii, 124, 171).

Aminohydroxysuccinic acid has been obtained by the action of barium nitrite on a solution of Lehrfeld's diaminosuccinic acid (Abstr., 1882, 163) in sulphuric acid solution, and was isolated as its *cupric* salt, $\text{C}_4\text{H}_5\text{O}_5\text{NCu}$. The acid melts at $314\text{--}318^\circ$ and has the meso-configuration as it is derived from *s*-dibromosuccinic acid, which can readily be transformed into meso-tartaric acid.

The aminohydroxy-acid described by Skraup (Abstr., 1904, i, 539) is probably the optically active or partially racemised acid.

J. J. S.

The Formation of Mercury Fulminate. LOTHAR WÖHLER and K. THEODOROVITS (*Ber.*, 1905, **38**, 1345—1351).—As stated by Stahl-schmidt (*Ann. Phys. Chem.*, 1860, **20**, 547), mercury fulminate may be prepared by the action of mercuric nitrate and nitric acid on the so-called "lignone," obtained by the dry distillation of wood; but the presence of nitrous fumes in the nitric acid used is essential for a successful result. Both methylal and acetal, preferably the latter, also yield mercury fulminate when treated in the same way as alcohol in the ordinary method. It is doubtful whether purified lignone is identical with methylal, as supposed by Dancer (*Annalen*, 1864, **132**, 240), as under certain conditions it behaves in the interaction differently from this substance. Acetaldehyde and its polymerides, paraldehyde and metaldehyde, readily yield pure mercury fulminate, but even in the most favourable circumstances, as in the case of alcohol, there is considerable waste of material. Methyl alcohol, formaldehyde, trioxymethylene, and formic acid do not give rise to mercury fulminate under any conditions; the same is true of substances containing three or more carbon atoms, such as propyl and isopropyl alcohols, allyl alcohol, propaldehyde, isobutaldehyde, acetone, and methyl ethyl ketone. Oximes, for example, acetaldoxime, do not generate mercury fulminate.

It thus appears that a chain of two carbon atoms is necessary for the formation of mercury fulminate; as the latter is not formed from

ethylene glycol, glyoxal, glyoxime, or acetonitrile, the following structures appear to be essential: $\cdot\text{CH}_2\cdot\text{OH}$, $\cdot\text{CH}\begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$, $\cdot\text{CHO}$, or $\cdot\text{CH}\cdot\text{O}\cdot$.

W. A. D.

Molecular Weight of Fulminic Acid. LOTHAR WÖHLER (*Ber.*, 1905, 38, 1351—1359).—The only real evidence in favour of the unimolecular formula for fulminic acid appears to be the three syntheses of fulminates by Nef (Abstr., 1895, i, 3), Jones (Abstr., 1898, i, 172), and Biddle (Abstr., 1900, i, 137); of these syntheses, the author could only successfully repeat that due to Nef.

Anhydrous sodium fulminate can be prepared in theoretical yield by the action of sodium amalgam on mercury fulminate suspended in absolute alcohol; it differs from the hydrated salt (Ebrenberg, Abstr., 1885, 1191), which is obtained pure only with great difficulty, in being quite stable at 100°. Measurements of its molecular weight in aqueous solution, taking into account the degree of dissociation, agree absolutely with the assumption of the formula CNOH for fulminic acid; the same view is supported by the difference, at 0°, of the equivalent conductivities of solutions of the salt at concentrations $N/32$ and $N/1024$.

The fact that a chain of two carbon atoms is necessary in the synthesis of mercury fulminate (preceding abstract) seemed to point to Steiner's bimolecular formula, $\text{C}_2\text{H}_2\text{O}_2\text{N}_2$, for fulminic acid being correct. It is, however, possible that the nitrous acid necessary in the production of mercury fulminate may give rise primarily to a nitrosyl derivative susceptible of easy decomposition. But an attempt, made from this standpoint, to prepare mercury fulminate by the action of mercury or its nitrate and nitric acid on ethyl nitroacetate was unsuccessful.

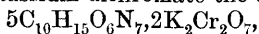
W. A. D.

Condensation Products from Glycoluril and Formaldehyde.

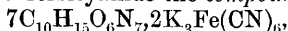
ROBERT BEHREND, EBERHARD MEYER, and FRANZ RUSCHE (*Annalen*, 1905, 339, 1—37).—In the preparation of glycoluril from glyoxal and carbamide, by-products are produced, especially when too small a quantity of carbamide is used: the compound $\text{C}_{11}\text{H}_{18}\text{O}_{10}\text{N}_6\cdot\text{H}_2\text{O}$, formed from carbamide (3 mols.) and glyoxal (4 mols.), is an amorphous, brownish-yellow substance; the compound $\text{C}_{20}\text{H}_{36}\text{O}_{19}\text{N}_{12}$, from carbamide (6 mols.) and glyoxal (7 mols.), is a brownish-yellow powder; both substances are soluble in alkali hydroxides.

When heated with formaldehyde in solution in hydrochloric acid, glycoluril condenses to form two compounds according to the quantity of formaldehyde used. The compound $\text{C}_{16}\text{H}_{18}\text{O}_6\text{N}_{12}$, formed from 3 mols. of glycoluril and 4 mols. of formaldehyde, is a white powder; it is converted by further treatment with formaldehyde into the compound $\text{C}_{18}\text{H}_{18}\text{O}_6\text{N}_{12}$, which is also formed directly from 3 mols. of formaldehyde and 1 mol. of glycoluril. The substance first mentioned is decomposed by warming with concentrated sulphuric acid, yielding the compound $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_7\cdot 2\text{H}_2\text{O}$, which crystallises in needles, losing water at 100°. This compound is exceedingly stable and forms a series of additive compounds with inorganic salts. With potassium

permanganate, it yields a *substance* crystallising in red or violet rods, with potassium bromide the *compound* $3\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot 2\text{KBr} \cdot 5\text{H}_2\text{O}$, crystallising in colourless rods, with ammonium chloride the *compound* $3\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot 2\text{NH}_4\text{Cl} \cdot 10\text{H}_2\text{O}$, forming regular crystals, with silver nitrate the *compound* $3\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot \text{AgNO}_3 \cdot 6\text{H}_2\text{O}$, crystallising in six-sided prisms, with chromic acid the *compound* $\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot \text{H}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$, forming ruby-red crystals, with potassium chromate the *compound* $2\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot \text{K}_2\text{CrO}_4 \cdot 5\text{H}_2\text{O}$, forming straw-yellow crystals, with potassium dichromate the *compound*



crystallising in orange-red needles, with potassium ferrocyanide the *compound* $7\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot 2\text{K}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, crystallising in white needles, with potassium ferricyanide the *compound*



crystallising in yellow rods, with platonic chloride the *compound* $7\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot 2\text{H}_2\text{PtCl}_6 \cdot 20\text{H}_2\text{O}$, crystallising in yellow prisms, and with sodium aurichloride the *compound* $\text{C}_{10}\text{H}_{15}\text{O}_6\text{N}_7 \cdot \text{NaAuCl}_4 \cdot 5\text{H}_2\text{O}$, forming golden-yellow crystals. Many organic dyes yield coloured precipitates with this compound.

Glycoluril does not condense with carbamide in alkaline solution, but the glycoluril is obtained from the mixture in the form of leaflets, and not in the usual needles or octahedra.

K. J. P. O.

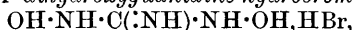
Condensation of *iso*Dialuric Acid with Thiocarbamide.

RICHARD BARTLING (*Annalen*, 1905, **339**, 37—40. Compare Abstr., 1901, i, 262).—By oxidation with nitric acid of the condensation product from *isodialuric* acid and thiocarbamide, Vogel (*loc. cit.*) has obtained a compound which was thought to be identical with dilituric acid. A more extended investigation has confirmed this supposition. It appears, however, that the compound produced is not the free acid, but the ammonium salt, $\text{C}_4\text{H}_6\text{O}_6\text{N}_4$; the salt is not decomposed by nitric acid. The identity of this salt with ammonium diliturate, prepared by other methods, was shown by crystallographic measurements and by the solubility in water. Characteristic ferrous and barium salts were also obtained.

K. J. P. O.

Cyanogen Bromide and Hydroxylamine. II.

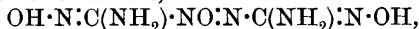
HEINRICH WIELAND (*Ber.*, 1905, **38**, 1445—1461. Compare Abstr., 1904, i, 628).—The reaction between cyanogen bromide and free hydroxylamine in alcoholic ethereal solution at the ordinary temperature is violent and almost explosive; it proceeds mainly according to the equation $2\text{CNBr} + 2\text{NH}_2 \cdot \text{OH} = \text{HCN} + \text{N}_2 + \text{CO}_2 + \text{NH}_4\text{Br} + \text{HBr}$. The reaction is largely modified by working at -20° with the compounds dissolved in a mixture of methyl alcohol and ether free from water, when a 75 per cent. yield of *dihydroxyguanidine hydrobromide*,



may be obtained. It is probably formed as follows: $\text{CNBr} + \text{NH}_2 \cdot \text{OH} = \text{CN} \cdot \text{NH} \cdot \text{OH} + \text{HBr}$; $\text{OH} \cdot \text{NH} \cdot \text{CN} + \text{NH}_2 \cdot \text{OH}, \text{HBr} = \text{OH} \cdot \text{NH} \cdot \text{C}(\text{:NH}) \cdot \text{NH} \cdot \text{OH}, \text{HBr}$, and may be freed from ammonium bromide by solution in methyl alcohol and ether. It crystallises in

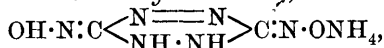
colourless, flat, hygroscopic needles, decomposes slowly at about 95°, rapidly at 120°, and is insoluble in benzene, ether, or chloroform. It is stable in the presence of acids and possesses strong reducing properties. With ferric chloride, its solutions give a bluish-black coloration, rapidly changing to green. When reduced with aluminium amalgam, it yields methylamine; with stannous chloride, ammonia. The blood-red alkaline solution changes to orange, and from this solution the following compounds have been isolated: azoxydicarbonamide dioxime, ammonium diisonitrosotetrahydrotetrazine, and hydrazodicarbonamide.

Azoxydicarbonamide dioxime,



is precipitated when the alkaline mixture is carefully treated with nitric acid. It crystallises from water at 60° as an orange-red powder, decomposing at 99°, is insoluble in organic solvents, and dissolves in hot water, but slowly decomposes. It gives a brownish-violet coloration with ferric chloride and does not show Thiele's azo-reaction (Abstr., 1892, 1429). As a base, it dissolves in acids, but the solutions immediately undergo decomposition. The *silver*, *lead*, and *mercuric* salts have been obtained as dark precipitates. On reduction with hydrogen sulphide, the azoxy-compound yields a readily soluble, colourless *hydrazo*-compound melting and decomposing at 190°.

Ammonium diisonitrosotetrahydrotetrazine,



is found in the filtrate from the azoxy-compound, and may also be obtained by the action of ammonia or sodium hydrogen carbonate on the salts of dihydroxyguanidine. It forms feathery, carmine-red crystals which explode at 158°; when acidified, a yellow solution of the free hydroxyl compound is obtained, but so far this has not been isolated. When warmed with acids, nitrous acid is formed, and this probably accounts for the fact that the compound gives Thiele's azo-reaction. Coloured precipitates of *silver*, *copper*, and *mercuric* derivatives have been obtained.

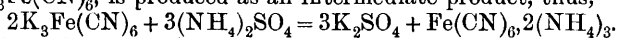
Hydrazodicarbonamide (Thiele, Abstr., 1892, 1298, 1429) usually accompanies the ammonium salt described above and is most readily obtained, together with potassium cyanate, by the action of alcoholic potassium hydroxide on dihydroxyguanidine.

Aminomethylnitrosolic acid, $\text{NO}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OH}$, obtained by the reaction of cyanogen bromide, hydroxylamine, and alcoholic potassium hydroxide, better by the action of methyl-alcoholic potash on dihydroxyguanidine hydrobromide or by the oxidation of the hydrobromide, crystallises from pure ether in large, flat, green plates, which decompose with violence at 38°. The *potassium* salt, $\text{CH}_2\text{O}_2\text{N}_3\text{K}$, crystallises from 80 per cent. alcohol in brilliant, steel-blue needles, which decompose at 213° or explode at 220°. It is not decomposed by dilute alkalis, but concentrated alkalis yield ammonia and hydrocyanic and carbonic acids. The *silver*, *copper*, *zinc*, and *ammonium* salts have been prepared and also a complex *mercuric* salt. The acid liberates iodine from acidified potassium iodide and sulphur from hydrogen sulphide, and like Piloty and von Schwerin's nitroso-compounds (Abstr., 1901, i, 516) may be used in place of nitrous acid for diazotising.

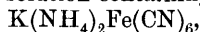
The *benzoate*, $\text{NO}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{O}\cdot\text{COPh}$, forms glistening, green plates, which melt and decompose at 119° . J. J. S.

Action of Oxalic Acid on Lead Ferrocyanide. AUGUSTE LEUBA (*Ann. Chim. anal.*, 1905, **10**, 143—145).—When lead ferrocyanide is boiled with solution of oxalic acid with free access of air, a golden-yellow liquid is obtained and an insoluble residue of mixed white and blue substances is formed. The latter consists of lead oxalate and Prussian blue, whilst the colour of the liquid is due to ferrous oxalate dissolved in excess of the oxalic acid. A strong odour of hydrogen cyanide is also perceptible. The reaction may be expressed by the following formulæ: (1) $\text{Pb}_2\text{Fe}(\text{CN})_6 + 2\text{C}_2\text{O}_4\text{H}_2 = 2\text{PbC}_2\text{O}_4 + \text{H}_4\text{Fe}(\text{CN})_6$; (2) $7\text{H}_4\text{Fe}(\text{CN})_6 + \text{O}_2 = 2\text{H}_2\text{O} + 24\text{HCN} + \text{Fe}_4[\text{Fe}(\text{CN})_6]_3$; (3) $\text{H}_4\text{Fe}(\text{CN})_6 + \text{C}_2\text{O}_4\text{H}_2 = 6\text{HCN} + \text{FeC}_2\text{O}_4$. L. DE K.

Action of Ammonium Chloride on Potassium Ferricyanide. JOH. MATUSCHEK (*Chem. Zeit.*, 1905, **29**, 439—440).—The cyanide, $\text{K}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$, is formed by the action of ammonium sulphate or of ammonium chloride on potassium ferricyanide, whilst the cyanide, $(\text{NH}_4)_3\text{Fe}(\text{CN})_6$, is produced as an intermediate product, thus,



By prolonged boiling of a solution containing the cyanide,



in presence of potassium ferricyanide and ammonium chloride, potassium ferrocyanide is produced owing to the dissociation of the ammonium chloride, thus,

$12[\text{K}_3\text{Fe}(\text{CN})_6] + 16\text{NH}_3 = 9[\text{K}_4\text{Fe}(\text{CN})_6] + 3[(\text{NH}_4)_4\text{Fe}(\text{CN})_6] + 4\text{N}$; the hydrogen chloride, formed by the dissociation of the ammonium chloride, liberates hydroferrocyanic and hydroferricyanic acids from their respective salts present, and then Prussian blue is formed.

A. McK.

Methylazoimide. OTTO DIMROTH and WILHELM WISLICENUS (*Ber.*, 1905, **38**, 1573—1576).—Crude sodium azoimide (Dennis and Browne, *Abstr.*, 1904, ii, 558) is dissolved in water, the solution, after being freed from ammonia by a current of air, is gently warmed in a reflux apparatus, and methyl sulphate added drop by drop; the methylazoimide evolved is passed over calcium chloride and soda-lime and condensed in a cooled U-tube. *Methylazoimide*, MeN_3 , is a colourless liquid, which boils at $20\text{--}21^\circ$, has an ethereal but unpleasant odour, explodes when heated above 500° , and has a sp. gr. $0\cdot869$ at $8^\circ/15^\circ$.

G. Y.

Organic Silicon Compounds. FRITZ TAURKE (*Ber.*, 1905, **38**, 1661—1670).—The following compounds are prepared by the interaction of silicon-chloroform and the corresponding alcohol.

Propyl orthosilicoformate, $\text{SiH}(\text{OPr})_3$, is a transparent, colourless, strongly-smelling liquid with a sweet taste; it boils at $191\text{--}192^\circ$ and has a sp. gr. $0\cdot885$ at $19\cdot5^\circ/4^\circ$. *Butyl orthosilicoformate* distils at

240—242°; *amyl orthosilicoformate* boils at 300—305° and has a sp. gr. 0.895 at 15°/4°.

Silicotetraisoamyl, $\text{Si}(\text{C}_5\text{H}_{11})_4$, prepared by the interaction of silicon tetrachloride, sodium, and *isoamyl chloride*, is a colourless, odourless liquid boiling at 275°. *Silicotriisoamyl hydride*, $\text{SiH}(\text{C}_5\text{H}_{11})_3$, is a colourless liquid boiling at 245°, which burns with a luminous flame; *silicotriisoamyl oxide*, $\text{Si}_2(\text{C}_5\text{H}_{11})_6\text{O}$, is a glycerine-like, colourless oil, which fluoresces faintly and distils at 360—370°. *Silicotriisoamyl bromide* is a heavy, yellow, fuming liquid boiling at 278—280°.

Triisoamylsilicol, $\text{OH}\cdot\text{Si}(\text{C}_5\text{H}_{11})_3$, prepared by the action of aqueous ammonia on the bromide, is a clear liquid of characteristic odour, boiling at 269—270°. *Silicotriisobutyl hydride* boils at 204—206°; the corresponding *bromide* is a yellow, fuming liquid, heavier than water, which boils at 245°.

Silicon tetrachloroethoxide, $\text{Si}(\text{OC}_2\text{H}_4\text{Cl})_4$, prepared by the interaction of glycol with silicon tetrachloride, whereby ethylenechlorohydrin is formed, and further treatment of this with silicon chloride, boils at 177—180° under 8 mm. pressure. *Silicon tetrachloropropoxide*, $\text{Si}(\text{OC}_3\text{H}_6\text{Cl})_4$, boils at 176° under 4 mm. pressure.

By the interaction of silicon chloride and ethylene glycol, a colourless, amorphous compound, $2\text{SiO}_2\cdot\text{C}_2\text{H}_4(\text{OH})_2$, is obtained.

Several statements with regard to silicon compounds in chemical literature are corrected. E. F. A.

Grignard's Reaction with Dihaloids. FELIX B. AHRENS and ADOLF STAPLER (*Ber.*, 1905, 38, 1296—1298. Compare Grignard and Tissier, *Abstr.*, 1901, i, 316).—The action of ethylene dibromide on magnesium in ethereal solution leads to the formation of the *additive* compound, $\text{C}_2\text{H}_4\text{Br}_2\cdot\text{Mg}\cdot\text{C}_4\text{H}_{10}\text{O}$, which separates in grey, transparent crystals, and yields ether and ethyl bromide with water, and the crystalline *additive* compound, $\text{MgBr}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}\cdot\text{C}_4\text{H}_{10}\text{O}$, when shaken with benzaldehyde in ethereal solution. In the presence of small quantities of iodine, the action leads to the formation of magnesium bromide and an *oil*, which, with benzaldehyde, forms $\text{MgBr}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{O}\cdot\text{MgBr}$, which is obtained as a yellow powder and melts at 160—164°. These magnesium derivatives of ethylene dibromide yield similar compounds with other aromatic aldehydes.

In ethereal solution, in presence of iodine, trimethylethylene dibromide and magnesium form a crystalline substance (magnesium bromide?) and an *oil*, which, with benzaldehyde, yields a white, crystalline *powder*, $\text{MgBr}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{CMe}_2\text{Br}$, sintering at 185°. G. Y.

Friedel and Crafts' Reaction. V. Formation of Dichlorodiphenylmethane by the Action of Carbon Tetrachloride on Benzene. JACOB BOESEKEN (*Rec. Trav. chim.*, 1905, 24, 1—5. Compare *Abstr.*, 1903, i, 617, and 1904, i, 384).—When benzene is added gradually to a mixture of aluminium chloride and carbon tetrachloride, a liquid *additive product* of dichlorodiphenylmethane and

aluminium chloride is formed, which on further treatment with benzene furnishes triphenylmethane chloride, and when washed with water yields dichlorodiphenylmethane. The yield of the latter by this process is from 80 to 90 per cent. of the theoretical.

Toluene under the same conditions yields a mixture of dichloroditolylmethanes in which the para-derivative predominates. With xylene, a certain amount of resinification occurs, but the crude product, when warmed with acetic acid, yields an oil which boils at 202° under 8 mm. pressure, and is probably 1 : 3 : 1' : 3'-tetramethylbenzophenone and may be identical with the dixylol ketone prepared by Rilliet and Ador (*J. pr. Chem.*, 1890, **41**, 9). With anisole, only traces of the corresponding dimethoxybenzophenone are produced, probably as the result of the formation of a resistant additive product of anisole and aluminium chloride.

T. A. H.

Friedel and Crafts' Reaction. VI. JACOB BOESEKEN (*Rec. Trav. chim.*, 1905, **24**, 6—18. Compare Abstr., 1900, i, 349; 1901, i, 474; 1903, i, 617, 626; 1904, i, 384; this vol., i, 268, and preceding abstract).—It is shown that this reaction can only proceed when the halogen atom of the haloid used can be rendered active by the catalytic agent. The activity and the quantity of the latter required in any particular case are determined by the possibility of the formation of additive compounds from the parent substances or the resulting product and the catalytic agent. Condensations illustrating these points are referred to in the original.

T. A. H.

Preparation and Nitration of *m*-Ethyltoluene. EDWARD BARTOW and A. W. SELLARDS (*J. Amer. Chem. Soc.*, 1905, **27**, 369—373).—A method is described for the preparation of *m*-ethyltoluene by a modification of the Fittig synthesis.

Dinitro-m-ethyltoluene, prepared by slowly adding *m*-ethyltoluene to fuming nitric acid cooled in a freezing mixture, forms an oil which undergoes decomposition when heated, but can be distilled with steam. On reduction with tin and hydrochloric acid, a small quantity of a diamine is formed which, when treated with nitrous acid, gives a compound analogous to Bismarck brown, thus indicating that the amino-groups are in the meta-position.

s-Trinitro-m-ethyltoluene, prepared by adding *m*-ethyltoluene to fuming nitric acid and warming the product with a mixture of fuming nitric and concentrated sulphuric acids, forms nearly colourless crystals and melts at 86° .

E. G.

***o*-Fluoronitrobenzene and other Aromatic Fluoro-derivatives.** M. HOLLEMAN (*Rec. Trav. chim.*, 1905, **24**, 26—32. Compare Abstr., 1904, i, 232 and 486, and this vol., i, 41).—*o*-Fluoronitrobenzene, prepared by oxidising with copper sulphate the 4-fluoro-3-nitrophenylhydrazine obtained by reducing the product of the diazotisation of 4-fluoro-3-nitroaniline, boils at 115.5° under 22 mm. pressure, solidifies on refrigeration, and then melts at -8° .

4-Fluoro-3-nitrobenzenesulphonic acid may be prepared by sul-

phonating fluorobenzene and nitrating the sulphonic acid obtained ; it is not altered by steam and sulphuric acid at 180—200°.

o-Fluorobenzoic acid may be prepared by the oxidation of *o*-fluorotoluene ; it melts at 119—120°, and does not lose the fluorine atom when heated with ammonia and calcium chloride at 200°.

T. A. H.

Iodoso-, Iodoxy-, and Iodonium Compounds from *s*-Iodoxylene. CONRAD WILLGERODT and FRIEDRICH SCHMIERER (*Ber.*, 1905, 38, 1472—1478).—Full details for the preparation of *s*-xylidine are given. A quantitative yield of aceto-4-*m*-xylidide is obtained when the base is boiled with 3 equivalents of acetic acid for 7 hours. A good yield of 6-nitro-2:4-dimethylacetanilide is obtained when the above acetyl derivative is nitrated with 5 times its weight of fuming nitric acid of sp. gr. 1.48 at a low temperature ; when hydrolysed with concentrated sulphuric acid for 10 minutes at 125°, it yields the corresponding nitroxylidine, from which the amino-group may be eliminated in the usual manner ; the *s*-nitroxylene thus obtained yields *s*-xylidine on reduction.

s-Iodoxylene yields a *dichloride*, $C_6H_3Me_2 \cdot ICl_2$, in the form of yellow, compact needles decomposing at 70°. When kept in a stoppered vessel, it loses the whole of its chlorine within 12—14 hours.

The *iodoso*-compound has been obtained in an amorphous form only. The *acetate*, $C_6H_3Me_2 \cdot I(OAc)_2$, crystallises in colourless prisms melting at 181°, the *basic sulphate*, $[C_6H_3Me_2 \cdot I(OH)]_2SO_4$, is extremely unstable and melts and decomposes at 120°. The *basic nitrate*, $C_6H_3Me_2 \cdot I(OH) \cdot NO_3$, forms a yellow powder decomposing at 122°.

s-Iodoxyxylene, $C_6H_3Me_2 \cdot IO_2$, crystallises from hot water in plates and explodes at 216°.

Di-s-xylilyliodonium hydroxide, $I(C_6H_3Me_2)_2 \cdot OH$, obtained by decomposing a solution of the iodide with silver oxide and evaporating in a desiccator, crystallises in beautiful white needles, and is the only iodonium hydroxide so far obtained as a solid.

The *iodide*, $I(C_6H_3Me_2)_2 \cdot I$, decomposes at 164°, the *bromide* crystallises in pale yellow leaflets and melts at 198°. The chloride melts at 186°, and the *dichromate*, $[I(C_6H_3Me_2)_2]_2Cr_2O_7$, forms orange-yellow plates and explodes at 172°.

Iodo-di-s-xylilyliodonium iodide, $I(C_6H_3Me_2)(C_6H_2IME_2) \cdot I$, obtained by Hartmann and Meyer's method (*Abstr.*, 1894, i, 242), forms yellow plates melting at 125°. The *bromide* melts at 149°, the *chloride* at 141°, and the *dichromate* explodes at 95°.

J. J. S.

Intramolecular Oxidation of a Thiol (SH) Group joined to a Benzene Nucleus by a Nitro-group in the ortho-Position. JAN J. BLANKSMA (*Rec. Trav. chim.*, 1905, 24, 46—52).—It is shown that in the conversion of trinitro-*ψ*-cumene into nitro-*ψ*-cumidine-sulphonic acid (Mayer, *Abstr.*, 1887, 659, 953), by the action of ammonium sulphide, ammonium nitrite is formed, and consequently one of the NO_2 - groups must be replaced without previous reduction by an -SH group (compare *Abstr.*, 1901, i, 460), which is subsequently

oxidised to $-\text{HSO}_3$ by the $-\text{NO}_2$ group in the ortho-position relative to it. This observation is confirmed by the fact that sodium hydrogen sulphide or sodium sulphide may be used in place of ammonium sulphide to effect the reduction.

Nitro- ψ -cumidinesulphonic acid, when heated with water in a closed tube at 180° , yields nitro- ψ -cumene; both these substances are converted by bromine in acetic acid into 2-bromo-5-nitro- ψ -cumidine, which crystallises in bright yellow needles and melts at 150° .

2:3:5-Trinitro- p -xylene behaves similarly when reduced with ammonium, sodium, or sodium hydrogen sulphides. The nitro- p -xylidinesulphonic acid so obtained (Fittig, Ahrens, and Mattheides, *Annalen*, 1867, 147, 24), when heated with water in a closed tube at 180° , yields nitro- p -xylidine. When trinitro- p -xylene is treated with sodium methoxide and methyl alcohol, it yields 3:5-dinitro-2-methoxy- p -xylene, $\text{OMe}\cdot\text{C}_6\text{HMe}_2(\text{NO}_2)_2$, which separates from alcohol in almost colourless needles, melts at 60° , and on nitration yields trinitromethoxy- p -xylene (m. p. 146°); the latter with ammonium sulphide yields 3-nitro-2-methoxy- p -xylidine-6-sulphonic acid, $\text{OMe}\cdot\text{C}_6\text{HMe}_2(\text{NO}_2)(\text{NH}_2)\cdot\text{SO}_3\text{H}$, which forms colourless crystals, melts at 252° , and, by heating with water at 180° in a closed tube, is converted into 3-nitro-2-methoxy- p -xylidine, melting at 98° . Trinitro- p -xylene, when warmed with methylamine (2 mols.) in alcohol in a closed tube, yields 3:5-dinitro-2-methylamino- p -xylene, which forms slender orange crystals and melts at 175° ; the corresponding ethylamino-derivative melts at 133° . Both these substances on nitration yield colourless, crystalline nitroamines melting at 94° and 36° respectively.

o -Nitrothiophenol is not reduced by ammonium sulphide, whence it appears that the reaction may be favoured by the presence of methyl groups in the nucleus; it is also accelerated by the action of light.

T. A. H.

Triphenylmethyl. XI. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1905, 38, 1333—1344. Compare *Abstr.*, 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244; 1904, i, 658, 988).—Triphenylmethyl combines with esters of the fatty acids to form compounds, probably of the type $\text{R}\cdot\text{CO}\cdot\text{OR}'(\text{CPh}_3)_2$, in which oxygen is quadrivalent. The compounds with propyl, isobutyl, and amyl formates, with methyl, ethyl, and propyl acetates, methyl, ethyl, propyl, and amyl propionates, methyl and ethyl butyrates, and with methyl valerate and ethyl carbonate were analysed. The hydrocarbon does not combine, however, with methyl and ethyl formates. Ethyl oxalate, methyl malonate, ethyl succinate, and ethyl benzoate also combine with triphenylmethyl in the proportion $(\text{CPh}_3)_2 : 1$ mol. ester. The compounds are crystalline, and are usually analysed by decomposing them at temperatures between 80° and 120° in a current of dry carbon dioxide, the residual triphenylmethyl being weighed. In the analysis of the less volatile esters, the triphenylmethyl is oxidised to the peroxide.

Crystalline compounds of triphenylmethyl with benzene, toluene, ethylbenzene, and the three xylenes were also prepared; in all cases, the product had the composition $(\text{CPh}_3)_2 + 1$ mol. hydrocarbon. Tri-

phenylmethyl also combines with a constituent of light petroleum, the product, which is only slowly decomposed in a vacuum, containing about 14 per cent. of the added substance; the nature of the latter is uncertain, but it approximates in composition to C_6H_{10} .

On adding amylene to a solution of triphenylmethyl in carbon disulphide, a crystalline *additive-compound*, $(CPh_3)_2 \cdot C_5H_{10}$, separates.

All the additive-compounds described, when subjected to the action of oxygen, give triphenylmethyl peroxide and the corresponding ester or hydrocarbon; they are probably therefore formed by a mere association of their constituents.

W. A. D.

Action of Sulphur on Aniline and Aniline Hydrochloride.

KARL A. HOFMANN (*Ber.*, 1905, 38, 1432—1433).—Hinsberg's dithioaniline (this vol., i, 339) has been previously obtained by the author (*Abstr.*, 1895, i, 87).

J. J. S.

Mode of Formation of Monosubstituted Urethane Derivatives.

F. BODROUX (*Compt. rend.*, 1905, 140, 1108—1109).—When ethyl carbonate is gradually added to an ethereal solution or suspension of the magnesium halogen compound of a primary aromatic amine, an energetic reaction takes place and a derivative of urethane is obtained. From aniline, ethyl phenylcarbamate is formed according to the equation: $2NHPh \cdot MgI + CO(OEt)_2 + H_2O = NHPh \cdot CO_2Et + NH_2Ph + OEt \cdot MgI + MgI \cdot OH$. The yield of ethyl phenylcarbamate is increased from 50 to 80 per cent. if the ether is boiled for several hours after the addition of the ethyl carbonate, or if the latter is added very slowly to the boiling ethereal solution. A small quantity of *s*-diphenylcarbamide is produced in the change according to the equation: $3NHPh \cdot MgI + CO(OEt)_2 + H_2O = CO(NHPh)_2 + NH_2Ph + 2OEt \cdot Mg \cdot I + OH \cdot MgI$.

o- and *p*-Toluidines and β -naphthylamine yield the corresponding urethanes by the same reaction. Ethyl carbonate has no action on the magnesium halogen derivative of ammonia.

H. M. D.

Reduction of Oximes and Hydrazones with Zinc Dust and Glacial Acetic Acid. HARTWIG FRANZEN (*Ber.*, 1905, 38, 1415—1417).—Benzaldoxime yields a mixture of benzylamine and dibenzylamine when reduced with zinc dust and glacial acetic acid in alcoholic solution. Similarly, from *o*-chlorobenzaldoxime a mixture of *o*-chlorobenzylamine and di-*o*-chlorobenzylamine is obtained. *o*-Chlorobenzylamine is a yellow oil, boiling at $103-104^\circ$ under 11 mm. pressure; the *hydrochloride* forms colourless plates melting at $215-216^\circ$; the *picrate* forms broad, yellow needles and melts and decomposes at 217° .

E. F. A.

Preparation of Certain Amines. LATHAM CLARKE (*Amer. Chem. J.*, 1905, 33, 496—500).—The following method is recommended for the preparation of dimethyl-*p*-toluidine. *p*-Toluidine is boiled with methyl iodide in a reflux apparatus for 30—40 minutes. The excess of methyl iodide is removed by distillation, the last portion being expelled by passing a current of air through the warm liquid.

The product is treated with a strong solution of potassium hydroxide, and the oily layer is separated and dried with solid potassium hydroxide. The oil is again treated with methyl iodide under the same conditions as before; the excess of methyl iodide is removed, potassium hydroxide solution is added to the residue, and the oil which separates is withdrawn and dried as before. On distilling the product, pure dimethyl-*p*-toluidine is obtained. Dimethyl-*o*-toluidine may be prepared in the same manner.

Methylisoamylamine, prepared by the above method, is a colourless liquid which boils at 95°.

Dimethylisoamylamine boils at 98° and has a strong odour.

The method has also been found to be of value for the preparation of benzyldimethylamine, but is not suitable for the preparation of α - and β -naphthyldimethylamines. E. G.

Evidence for the Possibility of Resolving an Optically Active Compound without actually Resolving it and without the Aid of Optically Active Substances. ERNST MOHR (*J. pr. Chem.*, 1905, [ii], 71, 305—357. Compare Abstr., 1904, i, 653; 1904, ii, 689; Kipping and Hall, *Trans.*, 1901, 79, 442; Kipping and Salway, *Trans.*, 1904, 85, 438).—This is chiefly a detailed account of work previously published.

When boiled with 6*N*-hydrochloric acid for 15 hours in a reflux apparatus, α -phenylethylamine is hydrolysed with formation of ammonia. Under the same conditions, ammonia is obtained also from benzhydrylamine (Darapsky, Abstr., 1903, i, 367).

Dihydrocinnamoylpiperidine, formed by the action of dihydrocinnamoyl chloride on piperidine in anhydrous ethereal solution, is obtained as a slightly yellow oil which partly solidifies. The *benzoin* ester of dihydrocinnamic acid, formed by fusing the acid chloride with benzoin or by boiling these substances with sodium carbonate in benzene solution, melts at 61—64°. The *benzylamide*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, formed by boiling the acid chloride with benzylamine and sodium carbonate in a neutral solvent, crystallises from hot alcohol or light petroleum in slender, white needles or narrow leaflets, or on slow evaporation in rosettes of plates. The α -phenylethylamide, formed in the same manner as the benzylamide, crystallises in white needles, is easily soluble in organic solvents, and is hydrolysed when boiled for 20 hours with 6*N*-hydrochloric acid, but not with alcoholic potassium hydroxide.

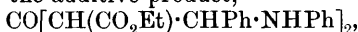
Ethyl benzylmalonate has n_D 1.487—1.490 at 13—19°; ethyl benzylethylmalonate boils at 173° under 12.5 mm. or at 184° under 18 mm. pressure, has n_D 1.488—1.490 at 13—19°, and on hydrolysis with alcoholic potassium hydroxide yields benzylethylmalonic acid, which forms a white, crystalline mass, melts at 104—114°, and commences to lose carbon dioxide at 128°. Benzylethylacetic acid is formed by heating the malonic acid at 145°, and finally at 180—190°; the chloride is best formed by the action of thionyl chloride on the acid.

The mixture of two racemic modifications of α -phenylethylamides of benzylethylacetic acid, obtained by the action of benzylethylacetyl chloride on α -phenylethylamine in presence of sodium carbonate in ethereal solution, yields on recrystallisation from light petroleum 15.6

per cent. of the less fusible and 55·8 of the more fusible isomeride. The modification melting at 112° crystallises in long, thin, white, glistening needles, is slightly soluble in cold light petroleum, but easily so in other organic solvents, has $[\alpha]_D$ less than +0·105°, and, when boiled for 37 hours or heated in a sealed tube at 110—132° for 21 hours, with hydrochloric acid of sp. gr. 1·093, is hydrolysed to the extent of 41 or 63 per cent. respectively, yielding benzylethylacetic acid, but only little α -phenylethylamine. The racemic modification melting at 87—88° crystallises in sheaves of slender, white, silky needles, is more easily soluble in light petroleum than is its isomeride, and is hydrolysed to the extent of 21 per cent. when boiled for 28 hours with hydrochloric acid of sp. gr. 1·093, or to 82 per cent. when heated with hydrochloric acid of sp. gr. 1·110 at 110—150° for 20·5 hours in a sealed tube.

G. Y.

Condensation of Benzylideneaniline with Ethylacetonedicarboxylate. CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], 33, 498—500. Compare Abstr., 1904, i, 832).—Schiff (Abstr., 1898, i, 237) has found that when ethyl acetonedicarboxylate is treated with benzylideneaniline the additive product,



is formed. The author has repeated this work, and finds that, when the reaction takes place in benzene solution, Schiff's additive product (m. p. 134°) is obtained, but that when alcohol is employed as a solvent the substance formed is probably *ethyl triphenylpiperidonedicarboxylate*, $\text{NPh} \begin{array}{c} \text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et}) \\ \text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et}) \end{array} \text{CO}$, although it may have the constitution $\text{NPh}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CHPh}$. This crystallises in large, colourless lamellæ, melts at 124°, and is very soluble in benzene or ether, less so in alcohol. This substance may also be obtained by boiling Schiff's additive product with alcohol. The author considers that Schiff's opinion that the additive product exists in three forms is not justified, and he points out that the same question has arisen with regard to the similar product formed with benzylideneaniline and ethyl acetoacetate (Rabe, Abstr., 1903, i, 62).

T. A. H.

Condensation of Phenol with Formaldehyde. FRITZ HENSCHKE (D.R.-P. 157553 and 157554).—When an alkaline solution of phenol is heated with formaldehyde at 100° in an autoclave, a solution is obtained which has strong antiseptic properties and is free from the odour of phenol. Acids precipitate a bulky, pale-yellow powder, insoluble in water or chloroform, soluble in alcohol, acetone, dilute sodium hydroxide, or ammonia. It decomposes on heating or on boiling its alkaline solution.

When iodine is added to the above alkaline solution, followed by an acid, a *compound* is obtained in which the iodine is combined organically.

C. H. D.

Picric Acid and 4:6-Dinitro-2-aminophenol (Picramic Acid). JULES ALOY and A. FRÉBAULT (*Bull. Soc. chim.*, 1905, [iii], 33, 495—498. Compare Abstr., 1904, i, 870).—Methods for the prepara-

tion of picramic acid from picric acid by the use of (1) zinc and ammonia solution and (2) sodium hyposulphite as reducing agents are described.

2-Chloro-4 : 6-dinitrophenol, prepared by Prud'homme and Rabaut's method (Abstr., 1892, 705), melts at 109°; it usually contains a small quantity of a crystalline substance which sublimes at 115—120°.

The first product of the diazotisation of picramic acid decomposes giving rise to a yellow, crystalline substance, which melts at 168—169° and is highly inflammable and explosive.

Picric acid may be detected in solutions containing only one part of the acid in 100,000 by the coloration produced on addition of sodium hyposulphite in presence of ammonia. T. A. H.

Dinitro-derivatives of *p*-Aminophenol. FRÉDÉRIC REVERDIN and AUGUSTE DRESEL (*Ber.*, 1905, 38, 1593—1599. Compare this vol., i, 51).—*Dinitro-p-acetylaminophenyl acetate*, formed by nitration of *p*-acetylaminophenyl acetate with nitric acid of sp. gr. 1.52 at -10°, crystallises in slender, white needles, melts at 223—224°, and is hydrolysed by acids to 3 : 5-dinitro-4-aminophenol, melting at 230—231°, by sodium carbonate in aqueous solution to 3 : 5-dinitro-4-acetylaminophenol melting at 182°.

3 : 2' : 4'-*Trinitro-4-hydroxydiphenylamine*, formed by heating 2-nitro-4-aminophenol with 1-chloro-2 : 4-dinitrobenzene in alcoholic solution, crystallises in orange leaflets, melts at 232—233°, and forms a yellow, crystalline sodium salt and an *acetyl* derivative which crystallises in lemon-yellow prisms and melts at 167—168°.

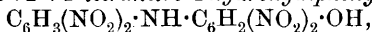
2 : 4-*Dinitrophenyl 3-nitro-4-aminophenyl ether* is formed by the action of 1-chloro-2 : 4-dinitrobenzene on 3-nitro-4-aminophenol in alcoholic solution; it crystallises in yellow leaflets and melts at 188°.

3 : 5-Dinitro-4-aminophenol crystallises in glistening leaflets or long, red needles, depending on the concentration of the solution, sublimes at 150°, and dissolves in aqueous alkali hydroxides or carbonates to a violet solution which becomes red and finally brown. With 1-chloro-2 : 4-dinitrobenzene it yields the *ether*, $C_6H_3(NO_2)_2 \cdot O \cdot C_6H_2(NO_2)_2 \cdot NH_2$, which crystallises in lemon-yellow needles, melts at 225—226°, and forms an *acetyl* derivative, $C_{14}H_9O_5N_5$, crystallising in needles and melting and decomposing at 238°. When stirred for some hours with sodium nitrite in cooled concentrated sulphuric acid solution, 3 : 5-dinitro-4-aminophenol forms the yellow, crystalline *diazonium* salt, which explodes when heated, and, when dried and boiled with absolute alcohol, yields 3 : 5-dinitrophenol (m. p. 122°).

2 : 5-Dinitro-4-acetylaminophenoxyacetic acid (Howard, Abstr., 1898, i, 29) is hydrolysed by sulphuric acid to 2 : 5-dinitro-4-aminophenoxyacetic acid, which crystallises in hexagonal, prismatic needles, or small, red prisms, commences to decompose at 190°, melts at 204—205°, does not react with chlorodinitrobenzene, and is converted into the *acetyl* derivative (m. p. 204—205°) when warmed with acetic anhydride and sulphuric acid; the *sodium* salt crystallises in red, glistening leaflets.

When diazotised in the same manner as 3 : 5-dinitro-4-aminophenol, *isopicramic* acid (Dabney, Abstr., 1884, 308; Meldola, Trans., 1902, 81, 988) forms explosive *diazonium* salts, which, when boiled with

absolute alcohol, yield 2:6-dinitrophenol (m. p. 64°) and are converted by cuprous chloride and potassium iodide into 4-chloro-2:6-dinitrophenol and 4-iodo-2:6-dinitrophenol respectively. *iso*Picramic acid and dinitrochlorobenzene, when boiled in alcoholic sodium acetate solution, form 3:5:2':4'-*tetranitro-4-hydroxydiphenylamine*,



which is a yellow, insoluble powder melting at 236° ; the *sodium* salt crystallises in brown needles; the *acetyl* derivative crystallises in yellow needles and melts at 210° . G. Y.

Nitration and Reduction of *s*-Dinitrophenetole. JAN J. BLANKSMA (*Rec. Trav. chim.*, 1905, **24**, 40—45. Compare *Abstr.*, 1903, i, 623).—When dinitrophenetole is warmed with nitric acid of sp. gr. 1.44 and sulphuric acid at 100° for 1 hour, 2:3:5-*trinitrophenetole* is formed; this separates from alcohol in bright yellow crystals and melts at 80° . Ammonia converts it into 3:5-*dinitro-2-phenetidine*, $\text{OEt} \cdot \text{C}_6\text{H}_2 \cdot \text{NH}_2(\text{NO}_2)_2$, which forms yellow crystals and melts at 195° . With methylamine, 3:5-*dinitro-2-methylaminophenetole* is produced; this forms orange crystals, melts at 174° , and on nitration furnishes the corresponding *nitroamine*, which is colourless and melts at 69° . 3:5-*Dinitro-2-ethylaminophenetole*, similarly obtained, forms orange crystals and melts at 137° ; the corresponding *nitroamine* melts at 72° . 3:5-*Dinitro-2-anilinophenetole*, $\text{OEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{NHPh}$, crystallises in yellow needles and melts at 155° .

2:3:5-Trinitrophenetole is converted by sodium ethoxide and ethyl alcohol into *dinitrocatechol diethyl ether*, which forms nearly colourless crystals and melts at 78° . On nitration, this yields 3:4:5-*trinitrocatechol diethyl ether*, which is colourless and melts at 122° . This substance may also be prepared by the direct nitration of catechol diethyl ether.

If 2:3:5-trinitrophenetole is warmed for 2 hours with nitric acid of sp. gr. 1.52 and sulphuric acid at 100° , 2:3:5:6-*tetranitrophenetole* is formed, which separates from alcohol in bright yellow crystals, melts at 115° , and is converted by sodium ethoxide and ethyl alcohol into *dinitrophloroglucinol triethyl ether*, $\text{C}_6\text{H}(\text{OEt})_3(\text{NO}_2)_2 = 1:3:5:2:6$ (compare *loc. cit.*).

On reduction with hydrogen sulphide in presence of ammonia, *s*-dinitrophenetole yields 3-nitro-5-*ethoxyaniline*, which crystallises from water in long, yellow needles, melts at 115° , and with bromine in acetic acid gives 2:4:6-*tribromo-3-nitro-5-ethoxyaniline*, which forms yellow crystals and melts at 102° .

s-Dinitroanisole, on reduction in the same way, yields 3-nitro-5-*methoxyaniline*, which forms orange crystals, melts at 118° , and furnishes a bright yellow *acetyl*-derivative melting at 193° ; the *tri-bromo*-derivative, prepared like the higher homologue, melts at 110° and yields 3:5-diaminoanisole on reduction with tin and hydrochloric acid.

T. A. H.

Attempts to Synthesise Fluorene Derivatives. OTTO DIELS and FELIX BUNZL (*Ber.*, 1905, **38**, 1486—1498. Compare *Ber.*, 1873, **6**, 187; Staedel, *Abstr.*, 1895, i, 147; Graebe and Ullmann, *ibid.*, 147).—Attempts have been made to prepare di-*o*-halogen derivatives

of diphenylmethane, and to transform these into fluorene derivatives by the removal of the halogen.

Ethyl sodiomalonate and ethyl sodioacetoacetate react with 1 : 2-dibromo-4-nitrobenzene (Hosaeus, Abstr., 1894, i, 17), yielding Staedel's 2-bromo-4-nitrophenetole (Abstr., 1883, 585). On hydrolysis with sulphuric acid, it yields 2-bromo-4-nitrophenol, which melts at 113—114°, and not at 102° as stated by Brunck (*Zeit. Chem.*, 1867, 204).

Formaldehyde condenses with *p*-bromophenetole in the presence of sulphuric acid at low temperatures, yielding 5 : 5'-dibromo-2 : 2'-diethoxydiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_3\text{Br}\cdot\text{OEt})_2$. It crystallises from acetic acid in well-developed prisms, melts at 143°, and dissolves readily in warm acetone or ethyl acetate, and in cold carbon disulphide or benzene. On oxidation with an acetic acid solution of chromic acid, it yields 5 : 5'-dibromo-2 : 2'-diethoxybenzophenone, which crystallises from alcohol in flat plates, melting at 99—100° and readily soluble in benzene or chloroform. The phenylhydrazone, $\text{C}_{23}\text{H}_{22}\text{O}_2\text{N}_2\text{Br}_2$, sinters at 130° and melts at 133°.

When hydrolysed with concentrated hydrochloric acid at 160—170°, or with aluminium chloride at 130—140°, it yields a compound, $\text{C}_{15}\text{H}_{12}\text{O}_3\text{Br}_2$, which has the composition of a monoethyl ether of dibromodihydroxybenzophenone, but its properties do not agree with such a constitution. It crystallises from acetic acid, melts at 114°, and yields a mono-potassium derivative, which is only stable in the presence of a large excess of alkali.

When boiled with aqueous alcoholic potash, it yields 2 : 7-dibromoxanthone (Perkin, *Trans.*, 1883, 43, 193).

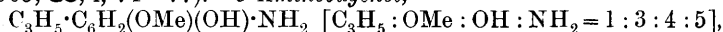
Details of the preparation of *m*-bromophenol are given (compare Wurster and Noetting, *Ber.*, 1874, 7, 905). When etherified by means of methyl sulphate and alkali, it yields *m*-bromoanisole as a colourless oil distilling at 210—211° under 752 mm. pressure. *m*-Bromoanisole and benzoyl chloride react with aluminium chloride in the presence of carbon disulphide yielding a mixture from which two substances have been isolated: a compound, $\text{C}_{14}\text{H}_{10}\text{O}_2\text{Br}_2$, which crystallises from alcohol, melts at 121° and dissolves sparingly in the usual organic solvents, and a compound, $\text{C}_{15}\text{H}_{12}\text{O}_2\text{Br}_2$, of phenolic nature, which distils at 305—310°.

J. J. S.

Action of Phosphorus on Organic Compounds. II. HERMANN WICHELHAUS (*Ber.*, 1905, 38, 1725—1728. Compare Abstr., 1903, i, 818).—Water and dinaphthyl oxide are formed by the action of hydrogen phosphide on α -naphthol at 200°, whilst naphthalene is formed at 300°. When α -naphthol is heated with yellow phosphorus at 300°, a mixture of naphthalene and dinaphthyl oxide is produced. Phosphorus chloride is formed when chloranil is heated with red phosphorus, and also a substance containing 44 per cent. of chlorine and yielding an acetyl derivative and an anilide.

A. McK.

5-Amino Eugenol. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1905, 35, i, 74—77).—5-Amino Eugenol,



best prepared by reducing benzeneazoeugenol with tin and hydrochloric acid, crystallises from light petroleum or water in shining, white scales, melting at 114° , and is soluble in acids or dilute alkali solutions, and readily so in the more common organic solvents. It undergoes a slight change in the air, assuming a grey colour, and is readily decomposed by concentrated hydrochloric acid. It decolorises bromine water or potassium permanganate solution and reduces Fehling's solution. The addition of a few drops of ferric chloride solution to its dilute hydrochloric acid solution yields a dark brown coloration which exhibits fluorescence in dilute solution. Its *hydrochloride* is white and melts at above 200° , and its *platinichloride* is obtained as a dark greenish-yellow, crystalline powder which does not melt or decompose at 230° . Its *acetyl* derivative, $C_{12}H_{15}O_3N$, crystallises from water in silky, white needles, melts at 132° and is very soluble in all organic solvents; it decolorises bromine water and permanganate solution, but yields no coloration with ferric chloride. Another acetyl derivative, melting at 86° , has also been obtained, but has not yet been examined.

T. H. P.

[2-Hydroxydibenzyl.] STANISLAUS VON KOSTANECKI (*Ber.*, 1905, 38, 1548).—2-Hydroxydibenzyl had been described by Stoermer (*Abstr.*, 1904, i, 181, 182) prior to the publication of Rost, Szabrański, and Kostanecki's paper (this vol., i, 341).

A. MCK.

Reactions of Certain Ethylenic Compounds with Mercuric Acetate in Glacial Acetic Acid Solution. Mercury Resorcinolmercuriacetate and Phloroglucinoltrimercuriacetate. ALEXANDRE LEYS (*J. Pharm. Chim.*, 1905, [vi], 388—396).—Benzenoid hydrocarbons, benzaldehyde, phenyl salicylate, phenolphthalein, and benzoic, cinnamic, phthalic, *o*-, *m*-, and *p*-hydroxybenzoic and picric acids give no precipitates with a warm solution of mercuric acetate in glacial acetic acid, but the hydroxybenzoic acids and phenolphthalein give faint rose colorations.

With monohydric phenols, dissolved in warm glacial acetic acid, a yellow colour is produced, and a white solid gradually separates. Catechol, quinol, and anthraquinone give brown colorations, mercuric acetate being deposited, whilst resorcinol at 60 — 70° gives a deep yellow precipitate.

Pyrogallol, phloroglucinol, and gallic acid give yellow, and tannin red, precipitates.

Aniline and toluidine give no reaction, but diazobenzenesulphonic acid and phenylhydrazine cause evolution of gas and the formation of yellow and red precipitates respectively.

The yellow *mercury resorcinolmercuriacetate*, $HgO_2 \cdot C_6H_3 \cdot Hg \cdot OAc$, decomposes on heating without fusing. It is insoluble in water, organic media, most salt solutions, alkalis, and dilute sulphuric and phosphoric acids, soluble in dilute hydrochloric and nitric acids, potassium cyanide, thiocyanate, bromide and iodide, sodium sulphite, thio-sulphate and hydrogen sulphide, mercuric sulphide separating from the two latter solutions, a reaction at once given by sodium sulphide.

With the solution in potassium iodide, iodine produces a violet precipitate unaltered by thiosulphate.

Phloroglucinoltrimercuriacetate, $C_6H_3(O \cdot Hg \cdot OAc)_3$, resembles the resorcinol compound in solubility, but is insoluble in dilute nitric acid, and iodine produces, in the potassium iodide solution, a brown colour discharged by thiosulphate.

G. D. L.

Influence of Alkaline Substances on Spontaneous Oxidation.

EDUARD SCHAER (*Arch. Pharm.*, 1905, **243**, 198—217. Compare Feder, this vol., i, 150).—As is well known, tannic acid, pyrogallol, quinone, aloin, chrysarobin, and brazilin are substances which undergo auto-oxidation, their solutions darkening in the air. This process is much accelerated by the presence of even small quantities of alkalis, of salts the solution of which in water has an alkaline reaction, and of alka'oids; a few mg. of these were added to each 10 c.c. of a dilute solution of the substance that undergo oxidation.

Special stress is laid on a suggestion that the darkening in colour observed when many pharmaceutical extracts are concentrated may be a consequence of the presence of ammonium nitrite, which Schönbein has shown to appear in water that is being evaporated. Besides effecting any specific oxidations characteristic of nitrites, it is one of those substances which accelerate auto-oxidation (its aqueous solution has an alkaline reaction).

C. F. B.

Conversion of Hydroaromatic Alcohols into Benzene Derivatives. KARL AUWERS [and, in part, M. HESSENLAND] (*Ber.*, 1905, **38**, 1697—1711. Compare Abstr., 1904, i, 26).—In the preparation of tertiary alcohols from cyclic ketones by the Grignard synthesis, it is advisable to use double the theoretical amount of magnesium alkyl iodide to carry out the reaction in concentrated solution and to immediately decompose with water.

1-Hydroxy-4-methyl-4-dichloromethyl-1-ethylidihydrobenzene, $C_{10}H_{14}OCl_2$, has been obtained in the form of colourless, compact prisms melting at 45—50°. When heated at 80° for 1—1.5 hours and then distilled under reduced pressure, it yields *1-methyl-4-dichloroisopropylbenzene*, $C_6H_4Me \cdot CHMe \cdot CHCl_2$, as a liquid distilling at 143—145° under 30 mm. pressure or at 247—249° under atmospheric pressure. It has a sp. gr. 1.1563 at 20°/20° and n_D 1.53356 at 20°. When reduced with sodium and boiling alcohol, it yields cymene, which was identified by conversion into pentabromotoluene melting at 280°, and hydroxycumic and *p-isopropenylbenzoic* acids.

When the methylchloroisopropylbenzene is oxidised with chromic anhydride, it yields *dichloro-p-cumic acid*, $CO_2H \cdot C_6H_4 \cdot CHMe \cdot CHCl_2$, in the form of flat needles melting at 113—114°, and when heated with water at 170—180° it is converted into an *aldehyde*, the *semicarbazone* of which melts at 157—159° and has the composition $C_{11}H_{15}ON_3$. The constitution of the aldehyde has not yet been determined.

An alcoholic solution of potassium hydroxide transforms the chloride into *β -chloro- α -p-dimethylstyrene*, $C_6H_4Me \cdot CMe \cdot CHCl$, which distils at 111—114° under 15 mm. pressure. When oxidised with permanganate, the styrene derivative is converted into *p-methylacetophenone*, the *semicarbazone* of which melts at 205°.

J. J. S.

Nitrobenzyl Ethers. GIOVANNI ROMEO (*Gazzetta*, 1905, 35, i, 111—120).—*p*-Nitrobenzyl methyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OMe}$, prepared by the action of sodium methoxide on *p*-nitrobenzyl chloride in methyl-alcoholic solution, separates from light petroleum in large prisms melting at $29\text{--}30^\circ$ and slowly turning green in the air, sublimes as a white powder, and is readily soluble in alcohol, benzene, or acetic acid.

p-Aminobenzyl methyl ether, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OMe}$, obtained by reducing a solution of the corresponding nitro-compound in sodium hydroxide by means of ferrous sulphate, is a dense, almost colourless oil distilling at $164\text{--}167^\circ$ under 40 mm. pressure and dissolves in water, alcohol, or ether; with oxalic acid in alcoholic solution it yields a white, crystalline oxalate melting at 116° .

p-Benzoylaminobenzyl methyl ether, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OMe}$, prepared by the action of benzoyl chloride on the previous compound in potassium hydroxide solution, crystallises from aqueous alcohol or a mixture of benzene and light petroleum in shining, silvery scales melting at $111\text{--}113^\circ$, and is readily soluble in alcohol or benzene and slightly so in light petroleum or water.

In preparing ethyl methyl malonate according to the method given by Züblin (*Abstr.*, 1879, 783), a small proportion of ethyl ethane-tetracarboxylate is also obtained.

Ethyl *p*-nitrobenzylmethylmalonate, prepared by the action of *p*-nitrobenzyl chloride on sodium ethyl methylmalonate, crystallises from alcohol or light petroleum in shining needles or monoclinic prisms melting at $59\text{--}60.5^\circ$, and is soluble in alcohol or benzene and to a moderate extent in light petroleum.

p-Nitrobenzylmethylmalonic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CMe}(\text{CO}_2\text{H})_2$, crystallises from xylene in scales or leaflets melting and decomposing at $162\text{--}163^\circ$, and is soluble in alcohol or water. It forms the following salts: *lead*, white precipitate; *silver*, white, gelatinous precipitate; *ferric*, whitish precipitate; *barium*, white, crystalline precipitate; *calcium*, white, acicular precipitate; *cupric*, pale blue precipitate, which crystallises from water in pale blue, silky needles containing $1\frac{1}{2}\text{H}_2\text{O}$. The xylene mother liquors from the above acid contain a small proportion of nitrophenylisobutyric acid (see Edeleanu, *Trans.*, 1888, 53 558), melting at 123° ; this acid is also formed on heating *p*-nitrobenzylmethylmalonic acid. T. H. P.

***o*- and *p*-Methoxyphenylethylcarbinols and the Corresponding Anetholes.** CARL HELL and ALEXANDER HOFMANN (*Ber.*, 1905, 38, 1676—1680).—*o*-Methoxyphenylethylcarbinol, prepared by the action of magnesium ethyl bromide on *o*-methoxybenzaldehyde, is a bright yellow, odourless oil boiling at 138° under 22 mm. and at 251° under 760 mm. pressure; the *phenylcarbamate* forms colourless crystals melting at 102° .

o-Anethole, prepared by distilling the carbinol with a little sulphuric acid, is a colourless oil with a characteristic odour, boiling at 222° ; it yields a yellow, crystalline *ψ*-nitrosite, $\text{C}_{20}\text{H}_{24}\text{O}_2 \cdot \text{N}_4\text{O}_6$, melting and decomposing at 123° , also a crystalline *nitrosochloride*, $\text{C}_{10}\text{H}_{12}\text{O} \cdot \text{NOCl}$. When care is taken to exclude all traces of acid

impurity during the preparation, *p*-methoxyphenylethylcarbinol is obtained as a colourless, viscous oil, boiling at 143° under 20 mm. and at 261° under the ordinary pressure (compare Klages, this vol., i, 344). E. F. A.

[*p*-Methoxyphenylethylcarbinol.] CARL HELL (*Ber.*, 1905, 38, 1680—1683).—Polemical (see preceding abstract, also Klages, *Abstr.*, 1904, i, 487, and this vol., i, 344). E. F. A.

Action of Magnesium Phenyl Bromide on Glycine Ethyl Ester. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1905, 38, 1686—1689. Compare Basset, this vol., i, 898).—Glycine ethyl ester (Fischer, *Abstr.*, 1901, i, 192) readily reacts with an excess of an ethereal solution of magnesium phenyl bromide, and the product, after treatment with hydrochloric acid, yields diphenyl and β -hydroxy- β -diphenylethylamine, $\text{OH}\cdot\text{CPh}_2\cdot\text{CH}_2\cdot\text{NH}_2$. The amine crystallises from hot water in colourless, glistening needles, melts at 110—111°, and is readily soluble in most organic solvents. The *hydrochloride* forms colourless needles melting at 192—193° and is readily soluble in water or alcohol. The *nitrate* melts at 203—204° and is only sparingly soluble in cold water or alcohol. The *picrate* melts at 183°; the *aurichloride*, $\text{C}_{14}\text{H}_{15}\text{ON}\cdot\text{HAuCl}_4$, crystallises with $1\text{H}_2\text{O}$, which it loses at 70—80°, and then melts at 119—120°; the *platinichloride* crystallises with $2\text{H}_2\text{O}$, melts at 155°, or in the anhydrous state at 161°. J. J. S.

Amino-alcohols of the Formula $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NX}_2$. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 157300. Compare *Abstr.*, 1904, i, 873; this vol., i, 127).—Aminoacetylcatechol and its derivatives may be reduced to amino-alcohols of the formula $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NX}_2$, which resemble the acetyl compounds in physiological properties, but are more active. Various methods of reduction may be employed. Thus aluminium powder and mercuric sulphate reduce methylaminoacetylcatechol sulphate; the *sulphate* of the resulting amino-alcohol is amorphous and gives a green coloration with ferric chloride. Ethylaminoacetylcatechol may be electrolytically reduced in 5 per cent. sulphuric acid solution, using lead electrodes with a diaphragm, and a current density of 0.25 amperes per sq. dm. at 2.5 volts. Sodium amalgam reduces aminoacetylcatechol, the amino-alcohol forming a hygroscopic *hydrochloride*. C. H. D.

Electrolytic Reduction of Aromatic Carboxylic Acids to the Corresponding Alcohols. CARL METTLER (*Ber.*, 1905, 38, 1745—1753).—When the solution of benzoic acid in a mixture of sulphuric acid and alcohol is electrolysed at 20—30° with lead electrodes and a current strength of 10 amperes, an 85 per cent. yield of benzyl alcohol is obtained. Similarly, *m*-bromobenzoic acid is converted into *m*-bromobenzyl alcohol, *m*-chlorobenzoic acid into *m*-chlorobenzyl alcohol, *o*-chlorobenzoic acid into *o*-chlorobenzyl alcohol, and *p*-chlorobenzoic acid into *p*-chlorobenzyl alcohol.

Anthranilic acid is converted into *o*-aminobenzyl alcohol, *m*-nitro-

benzoic acid into *m*-aminobenzyl alcohol, and *m*-hydroxybenzoic acid into *m*-hydroxybenzyl alcohol. Phenyl benzoate is readily converted into phenylbenzyl ether and benzyl benzoate into dibenzyl ether.

A. McK,

Salts of Benzamide with Dicarboxylic Acids. FRANZ HENLE (*Ber.*, 1905, **38**, 1373—1375).—The following salts are easily obtained by dissolving benzamide and the acid in hot water or, better, in alcohol. *Benzamide oxalate*, $2\text{COPh}\cdot\text{NH}_2\cdot\text{C}_2\text{H}_2\text{O}_4$, crystallises from water in white leaflets and melts at 156—157°. *Benzamide tartrate*, $2\text{COPh}\cdot\text{NH}_2\cdot\text{C}_4\text{H}_6\text{O}_6$, crystallises from alcohol in leaflets and melts at 137—140°. *Benzamide succinate*, $\text{C}_{11}\text{H}_{13}\text{O}_5\text{N}$, crystallises in colourless prisms and melts at 126—128°. An oxalate of diphenylamine could not be obtained.

W. A. D.

Reduction of Benzonitrile and *p*-Tolunitrile. A. FREBAULT (*Compt. rend.*, 1905, **140**, 1036—1038).—By the direct hydrogenation of aromatic nitriles in presence of reduced nickel at 200°, Sabatier and Senderens (this vol., i, 267) obtained only the corresponding hydrocarbons and ammoma. Under modified experimental conditions the author finds that the reaction is similar to that which takes place with the aliphatic nitriles and that primary and secondary aromatic amines can be thus obtained. To ensure uniformity of temperature, the tube containing the reduced nickel is imbedded in iron filings, and a rapid current of hydrogen is passed through it at about 250°, the nitrile being allowed to fall directly into the tube drop by drop.

From benzonitrile, benzylamine and dibenzylamine are obtained in approximately equal quantities, together with a small quantity of crystals, possibly tribenzylamine. From *p*-tolunitrile, *p*-methylbenzylamine and di-*p*-methylbenzylamine are obtained.

H. M. D.

Condensation Product from Anthranilic Acid and Formaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158090).—Anthranilic acid is precipitated from its aqueous solutions, even when very dilute, in the form of a condensation product insoluble in alkali hydroxides. This compound forms large, yellowish-white crystals, which decompose slowly at 150°, and dissolve sparingly in alcohol or hot benzene. The crystals are strongly luminous when rubbed in the dark. Hydrocyanic acid converts it into ω -cyanomethylantranilic acid.

C. H. D.

Derivatives of Anthranilic Acid. BRONISLAW VON PAWLEWSKI (*Ber.*, 1905, **38**, 1683—1685. Compare *Abstr.*, 1904, i, 316).—*N*-Phenylsulphoneanthranilic acid, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, obtained by heating a xylene solution of anthranilic acid and benzenesulphonic chloride, crystallises from acetic acid in thick, colourless needles, melts at 214—215°, has sp. gr. 1.4255 at 20°/4°, and is only sparingly soluble in the usual organic solvents.

N-Chloroacetyl anthranilic acid, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, crystallises from alcohol in long, slender needles melting at 186—188°.

N-Piperonylene-anthranilic acid, $\text{CH}_2 \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, after crystallisation from alcohol, forms yellow needles and prisms melting at $192-193^\circ$. It is sparingly soluble in toluene, but dissolves in ammonia yielding a colourless solution.

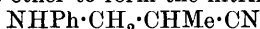
N-p-Aminobenzylidene-anthranilic acid,
 $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, crystallises from alcohol in dark red prisms, melting and decomposing at $225-227^\circ$. Its solution in ammonia is colourless.

N-p-Nitrobenzylidene-anthranilic acid crystallises from alcohol in colourless plates melting at $165-167^\circ$. J. J. S.

Preparation of Nitriles. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 157617).—Schiff's bases, and also the polymolecular condensation products from aromatic amino-compounds and aliphatic or aromatic aldehydes, react on warming with a dilute solution of hydrocyanic acid in water or dilute alcohol to form nitriles of the general formula $\text{NHR} \cdot \text{CHR}' \cdot \text{CN}$, where R is an aromatic group, and R' hydrogen or an alkyl or aryl group. The temperature of reaction varies in different cases, closed vessels being employed to avoid loss of hydrocyanic acid. Thus, the anhydro-base from *p*-toluidine and formaldehyde yields *ω*-cyanomethyl-*p*-toluidine, melting at 62° , and in the same way *ω*-cyano-*o*-chlorobenzylaniline, melting at 77° , *ω*-cyanobenzyl-anthranilic acid, melting at 175° , and *ω*-cyanoethylanthranilic acid, melting at 192° , may be prepared.

Benzylidene-α-naphthylamine, from benzaldehyde and *α*-naphthylamine, melts at $73-74^\circ$ and yields *ω*-cyanobenzyl-*α*-naphthylamine, melting at $116-117^\circ$, with hydrocyanic acid. In similar manner, benzylidene-*β*-naphthylamine yields *ω*-cyanobenzyl-*β*-naphthylamine, melting at 115° . C. H. D.

Preparation of Nitriles. HANS BUCHERER (D.R.-P. 157710, 157840, 157909, and 157910. Compare Abstr., 1902, i, 533; 1903, i, 612, and preceding abstract).—Ketones react with derivatives of aromatic amines of acid reaction and metallic cyanides to form nitriles in presence of an indifferent solvent. The amine salt must be capable of setting free hydrogen cyanide, at the same time losing its acid reaction. Thus acetone, aniline hydrochloride, and potassium cyanide react together in moist ether to form the nitrile,



(Tiemann, Abstr., 1883, 199). The reaction takes place in light petroleum solution without the addition of water. Benzaldehyde and formaldehyde react in the same manner as acetone.

The sodium hydrogen sulphite compounds of Schiff's bases of the naphthalene series, like the corresponding benzene compounds, yield nitriles with potassium cyanide.

ω-Cyanomethyl-*β*-naphthylamine, from the sodium hydrogen sulphite compound of anhydroformaldehyde-*β*-naphthylamine, melts at 105° .

It is also possible to prepare nitriles of the same type without isolation of the Schiff's bases, avoiding the presence of an excess of sulphurous acid, which gives rise to loss of hydrogen cyanide (compare

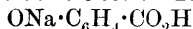
Eibner, Abstr., 1901, i, 376). Thus, molecular quantities of formaldehyde, sodium hydrogen sulphite, and aniline are warmed at 90° . After a few minutes, potassium cyanide is added and ω -cyanomethyl-aniline immediately separates. In the case of β -naphthylamine, some naphthacridine is formed, and is removed by filtration before the addition of potassium cyanide.

Acetaldehyde reacts in the same way as formaldehyde and benzaldehyde.

Details of the preparation of several nitriles are given.

C. H. D.

Introduction of Carboxyl Groups into Phenol by the Action of Carbon Dioxide. I. **Salicylic Acid.** S. TIJMSMA, jun. (*Ber.*, 1905, 38, 1375--1385).—The immediate product obtained by heating sodium phenoxide with carbon dioxide at 120 – 130° under pressure is *o*-sodoxybenzoic acid (*sodium phenoxide-o-carboxylic acid*), $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and is not identical with sodium salicylate. This is shown by its having a considerably greater dissociation tension than sodium salicylate by the fact that, unlike the latter, it slowly absorbs dry ammonia gas at the ordinary temperature and by its violently decomposing with evolution of carbon dioxide when thrown into petroleum at 170 – 180° , whereas sodium salicylate requires a temperature of 230° to produce the same effect. The compound



is not transformed into sodium salicylate by boiling with water and evaporating to dryness or by being heated alone in a sealed tube for 4 hours at 248° ; on the other hand, it is completely converted into this salt by dissolution in acetone. *o*-Sodoxybenzoic acid, when heated with methyl iodide during 2 days at 140 – 150° , gives methyl salicylate, although pure sodium salicylate under the same conditions is not changed, but the presence of a little disodium salicylate enables sodium salicylate also to interact with methyl iodide, giving methyl salicylate. The formation of this ester from *o*-sodoxybenzoic acid is probably due to the transformation of the *o*-methoxybenzoic acid originally formed under the influence of *o*-sodoxybenzoic acid; it is shown that a trace of the latter is sufficient to convert *o*-methoxybenzoic acid, when heated at 140 – 150° for 24 hours, into its isomeride. Sodium salicylate, when heated for $2\frac{1}{2}$ hours in a sealed tube at 248° , undergoes a more or less complete change into *o*-sodoxybenzoic acid.

The foregoing facts show that in the production of salicylic acid by Kolbe's synthesis the carbon dioxide directly enters the nucleus; contrary to the usually accepted view, sodium phenyl carbonate cannot play any essential part in the synthesis, as it completely decomposes into its constituents at a temperature of 85° . The peculiar transformation of *o*-sodoxybenzoic acid in acetone solution and its stability in presence of water are discussed at some length.

W. A. D.

Brominated cycloPropanedicarboxylic Acids. EDUARD BUCHNER and WILHELM WEDEMANN (*Ber.*, 1905, 38, 1599–1602. Compare Buchner, Abstr., 1895, i, 269).—When heated with bromine and red

phosphorus in a sealed tube at 150—160° for 6—8 hours, *cis*- or *trans*-cyclopropane-1 : 2-dicarboxylic acid yields two isomeric dibromo-derivatives.

a-Dibromocyclopropane-1 : 2-dicarboxylic acid, $C_5H_4O_4Br_2$, crystallises in small, colourless prisms, and when rapidly heated becomes grey at 220°, darkens at 275°, and melts and decomposes at 282°. It is only slightly soluble in chloroform, but dissolves readily in ether or alcohol, and is stable towards alkaline permanganate.

β -Dibromocyclopropane-1 : 2-dicarboxylic acid crystallises in small, colourless, glistening prisms, melts at 202°, is more soluble than the *a*-isomeride in water or organic solvents, and does not decolorise alkaline permanganate solution.

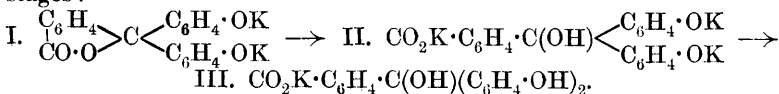
When reduced with sodium amalgam in aqueous solution, both dibromo-acids yield *trans*-cyclopropane-1 : 2-dicarboxylic acid, G. Y.

Constitution of the Phthalein Salts. RICHARD MEYER and OSKAR SPENGLER (*Ber.*, 1905, **38**, 1318—1333).—A reply is given to Green and Perkin's criticisms (*Trans.*, 1904, **85**, 398) of a previous paper (*Abstr.*, 1903, i, 833), the lactonoid structure for quinolphthalein salts being still maintained. When phenolphthalein is digested with an excess of *N*-sodium hydroxide solution, the salt which is dissolved has the composition $C_{20}H_{12}O_4Na_2$; similarly, quinolphthalein and phenolphthalein anilide behave as dibasic acids, giving respectively the salts $C_{20}H_{10}O_5Na_2$ and $C_{20}H_{12}O_3Na_2 \cdot NPh$. These facts point to phenolphthalein having in its red alkaline solutions the same lactonoid structure which quinolphthalein and phenolphthalein anilide are admitted to have because they give colourless solutions with alkalis. Attempts were made to obtain evidence of the formation of a coloured quinonoid ether by methylating the alkali salts of phenolphthalein or quinolphthalein; but whether the methylation is effected by methyl iodide or methyl sulphate, in aqueous or alcoholic solution, with an excess of alkali or with sodium methoxide, the ordinary colourless, lactonoid dialkyl ethers of the type $\begin{matrix} C_6H_4 \\ CO \cdot O \end{matrix} > C(C_6H_4 \cdot OMe)_2$ are obtained.

The normal sodium salts of the phthaleins give, on methylation, however, in addition to the dialkyl ethers, colourless, mono-alkyl ethers having the formulæ $\begin{matrix} C_6H_4 \\ CO \cdot O \end{matrix} > C(C_6H_4 \cdot OH) \cdot C_6H_4 \cdot OMe$ and

$\begin{matrix} C_6H_4 \\ CO \cdot O \end{matrix} > C \begin{matrix} < C_6H_3(OMe) \\ < C_6H_3(OH) \end{matrix} > O$ respectively; these substances form red alkali salts similar to those of the parent phthaleins. As the quinonoid formula for the phthaleins contains one carboxyl and one hydroxyl group, and the lactonoid formula two phenolic hydroxyl groups, the behaviour of benzoic acid and of phenol when methylated under the same conditions as the phthaleins was studied. Phenol is converted under all conditions, using methyl iodide or methyl sulphate in neutral, acid or alkaline solution, into its methyl ether; benzoic acid, on the other hand, gives rise to its ester only in acid solution, and not in presence of alkali even when methyl sulphate is employed. It is difficult to reconcile these facts with the quinonoid formula for the phthaleins.

It is considered that the formation of the colourless carbinol salt, $\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{C}_6\text{H}_4 \cdot \text{OH})_2$, of phenolphthalein (Green and Perkin, *loc. cit.*) does not support the quinonoid formula for the coloured phthalein salts; it may be produced equally well by the following stages:

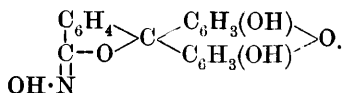


The coloured solution contains the salt I, which is transformed into the salt II by an excess of alkali; on adding acetic acid until the solution is neutral, the colourless salt III is formed.

Attempts to oxidise the ester, $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} > \text{O}$, derived from quinolphthalein, by means of potassium ferricyanide in slightly alkaline solution, to a true quinonoid derivative failed.

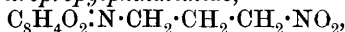
The coloured β -oxime of quinolphthalein decomposes barium carbonate, forming the *barium* salt, $(\text{C}_{20}\text{H}_{12}\text{O}_5\text{N})_2\text{Ba} \cdot 2\text{H}_2\text{O}$, which crystallises in small, yellow nodules. The *barium* salt of the isomeric γ -oxime forms aggregates of small, yellow needles and is anhydrous. On boiling the β -oxime in alcoholic solution with dilute sulphuric acid during several days, it is transformed into the γ -oxime. It is probable

that the two oximes have the structure $\begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C} - \text{O} \end{array} > \text{C} < \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} > \text{O}$ and $\begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C} - \text{O} \\ | \\ \text{N} \cdot \text{OH} \end{array} > \text{C} < \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} > \text{O}$ and



W. A. D.

γ -Nitropropylphthalimide. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 1692—1693).— *γ -Nitropropylphthalimide*,



obtained by heating γ -iodopropylphthalimide with a mixture of silver nitrite, sea-sand, and absolute ether at 100° , crystallises from alcohol in glistening needles, melts at 83 — 84° , and may be distilled under reduced pressure.

When hydrolysed at 130 — 140° with concentrated hydrochloric acid, it yields phthalic acid, hydroxylamine, and a small amount of β -alanine.

J. J. S.

Reduction Products of Di-*p*-nitrobenzylmalononitrile.

GIOVANNI ROMEO and C. MARCHESE (*Gazzetta*, 1905, 35, i, 121—131).—*Di-p-aminobenzylmalononitrile*, $\text{C}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2(\text{CN})_2$, prepared by reducing di-*p*-nitrobenzylmalononitrile with tin and hydrochloric acid, separates from benzene in crystals melting at 161 — 163° and from alcohol in needles which contain $1\text{C}_2\text{H}_6\text{O}$ and melt at 159 — 161° ; it is slightly soluble in water. Its *hydrochloride*, $\text{C}_{17}\text{H}_{16}\text{N}_4 \cdot 2\text{HCl}$, is precipitated in the form of small needles melting at above 300° , and is very readily soluble in water and slightly so in hydrochloric acid. The *platinichloride*, $\text{C}_{17}\text{H}_{16}\text{N}_4 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, forms a yellow, crystalline precipitate; it is reduced when heated in water or alcohol, and burns

without melting when heated on platinum. The *mercurichloride* forms aggregates of needles and melts and decomposes at 204—206°.

Dichlorodi-p-aminodibenzylmalononitrile, $C(CH_2 \cdot C_6H_4Cl \cdot NH_2)_2(CN)_2$, occasionally formed along with di-*p*-aminobenzylmalononitrile on reducing di-*p*-nitrobenzylmalononitrile with tin and hydrochloric acid, crystallises from alcohol or xylene in starry aggregates of small needles melting at 200—201°, and dissolves in hydrochloric acid giving an unstable hydrochloride.

Di-p-acetylaminobenzylmalononitrile crystallises from alcohol or aqueous acetic acid in silvery scales melting at 258—260°.

Tetrabromodi-p-aminodibenzylmalononitrile,
 $C(CH_2 \cdot C_6H_3Br_2 \cdot NH_2)_2(CN)_2$,
 crystallises from benzene or xylene in tufts of white needles melting at 279—281° and decomposing at 285°, and is insoluble in acids owing to the presence of bromine in the molecule.

Tetrabromodi-p-acetylaminodibenzylmalononitrile crystallises from alcohol in small needles melting at 205—206°, and is soluble in benzene. When heated with an aqueous alcoholic solution of sodium hydroxide, it yields ammonia and *tetrabromodi-p-aminodibenzylcyanoacetic acid*, $CO_2H \cdot C(CN)(CH_2 \cdot C_6H_3Br_2 \cdot NH_2)_2$, which separates from alcohol in badly-defined crystals melting at 238°, and is moderately soluble in acetic acid and slightly so in xylene; it is a weak acid which dissolves readily in alkali hydroxide solutions, but with difficulty in alkali carbonate solutions. Its *amide*, prepared by reducing di-*p*-aminobenzylmalononitrile with sodium in alcoholic solution, crystallises from alcohol in slender needles melting at 231°. T. H. P.

Derivatives of the Iodobenzaldehydes containing Uni- and Ter-valent Iodine. CONRAD WILLGERODT and REINHOLD RIEKE (*Ber.*, 1905, 38, 1478—1486. Compare Patterson, *Diss.*, 1896).—The *semicarbazones* of *o*-, *m*-, and *p*-iodobenzaldehydes crystallise in colourless needles and melt respectively at 206°, 225—226°, and 224·5°. The *iodobenzylideneazines*, $C_6H_4I \cdot CH \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} CH \cdot C_6H_4I$, obtained by the action of hydrazine sulphate on the iodoaldehydes, crystallise in yellow needles and melt at 184·5°, 146·5°, and 231° respectively. The *iodobenzylidene-benzidines*, $C_{12}H_8(N \cdot CH \cdot C_6H_4I)_2$, form golden-yellow plates and melt at 252—253°, 235°, and above 360°.

Iodinium compounds have been obtained from the *m*- and *p*-iodoaldehydes, but not from the ortho-compound. These compounds were prepared by Meyer and Hartmann's method, and also by Willgerodt's method from the dichlorides and mercury diphenyl.

Salts of *benzaldehydephenyliodinium hydroxide* :

	<i>Meta.</i>	<i>m. p.</i>	<i>Para.</i>	<i>m. p.</i>
<i>Chloride</i>	Colourless needles	167°	Colourless prisms	183°
<i>Bromide</i>	„	165	„ needles	157
<i>Iodide</i>	„	142	„	143
<i>Nitrate</i>	„	163 dec.	—	—
<i>Pyrochromate</i>	Yellow needles	dec.	Yellow crystals	151 dec.
<i>Platinichloride</i>	Prisms	169 dec.	Yellow prisms	180 dec.
<i>Mercurichloride</i> ..	Colourless	dec.	Colourless crystals	172 dec.

A number of condensation products of *m*- and *p*-benzaldehydophenyl-iodinium iodides have been obtained :

	<i>Meta.</i>	<i>m. p.</i>	<i>Para.</i>	<i>m. p.</i>
<i>Semicarbazone</i>	Colourless prisms	204°	Colourless needles	212°
<i>Phenylhydrazone</i> ...	Yellow crystals	156	Yellow crystals	144
<i>Benidine compound</i>	Yellow plates	228—229	Yellow plates	above 360

J. J. S.

Condensation of Aldehydes with Ketones. EDMUND O. VON LIPPMANN and RODOLFO FRITSCH (*Ber.*, 1905, **38**, 1626—1630).—

Stilbeneacetone (1 : 2-diphenyl- Δ^1 -cycloventene-4-one), $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CPh} \\ | \\ \text{CH}_2 \cdot \text{CPh} \end{smallmatrix} >$, obtained by the condensation of benzaldehyde and acetone by means of zinc chloride, separates from a mixture of alcohol and ether as a yellowish-brown, crystalline precipitate softening at 167°, and is readily soluble in ether, chloroform, carbon disulphide, benzene, toluene, ethyl acetate, or acetic acid. When heated, 3 mols. of stilbeneacetone condense, with loss of $2\text{H}_2\text{O}$, to form *tristilbeneacetone-anhydride*, $\text{C}_{51}\text{H}_{38}\text{O}$, which can be more readily obtained by heating the original mixture of benzaldehyde, acetone, and zinc chloride for 10 hours at 200°, and separates from acetic acid in crystals melting at 188°, and is moderately soluble in ether, acetone, or chloroform.

Dipropylstilbeneacetone, $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4\text{Pr} \\ | \\ \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4\text{Pr} \end{smallmatrix} >$, prepared by the action of cuminaldehyde on acetone in presence of zinc chloride, separates from a mixture of chloroform and alcohol in pale yellow crystals melting at 158°, and is readily soluble in ether, chloroform, benzene, toluene, or ethyl acetate.

Dihydroxystilbeneacetone anhydride, $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{smallmatrix} > \text{O}$, prepared by the condensation of salicylaldehyde with acetone in presence of zinc chloride, melts at 215° and is soluble in most solvents except light petroleum.

Dimethoxystilbeneacetone, $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \\ \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \end{smallmatrix} >$, prepared from anisaldehyde and acetone, separates in pale brown crystals melting at 129°, and dissolves in the same solvents as the preceding compound.

Distyrylethyleneacetone, $\text{CO} < \begin{smallmatrix} \text{CH}_2 \cdot \text{C} \cdot \text{CH} : \text{CHPh} \\ | \\ \text{CH}_2 \cdot \text{C} \cdot \text{CH} : \text{CHPh} \end{smallmatrix} >$, obtained by the condensation of cinnamaldehyde with acetone in presence of zinc chloride, separates from a mixture of benzene and light petroleum in yellowish-brown crystals melting at 208°. T. H. P.

Preparation of cycloHexanol, cycloHexanone, and Derivatives. ARNOLD F. HOLLEMAN, F. H. VAN DER LAAN, and H. J. SLIJPER (*Rec. trav. chim.*, 1905, **24**, 19—24. Compare *Abstr.*, 1904, i, 40).—The crude product obtained by passing dry hydrogen, impregnated with phenol vapour, over reduced nickel heated at 140—150° contains

water, *cyclohexene*, *cyclohexanol*, and *cyclohexanone*. The two former may be isolated by fractional distillation. From the residue, *cyclohexanone* may be removed by the addition of sodium hydrogen sulphite, or more completely by conversion into dibenzylidenecyclohexanone by the action of benzaldehyde in presence of sodium hydroxide, leaving *cyclohexanol*, which may be purified by desiccation over lime and distillation; it boils at 159–160°, solidifies when cooled, and melts at 20°.

Sabatier and Senderens' method (Abstr., 1904, i, 156) of preparing *cyclohexanone* from the mixture by passing the vapour over copper heated to 330° results in the production of *cyclohexene*, *cyclohexane*, and benzene, and a better yield of the ketone is obtained when the copper is heated to 280° and the vapour is mixed with a small quantity of air. The preparation of adipic acid and of *cyclopentanone* (Hentzschel and Wislicenus, Abstr., 1893, i, 555) from the mixture of *cyclohexanol* and *cyclohexanone* is described.

T. A. H.

Ketens. HERMANN STAUDINGER (*Ber.*, 1905, 38, 1735–1739).—*Diphenylketen*, CPh_2CO , the first representative of a new type of compound, is prepared by the action of zinc on an ethereal solution of diphenylchloroacetyl chloride; it boils at 146° under 12 mm. pressure, has the colour of a concentrated solution of potassium dichromate, and solidifies in a freezing mixture to a mass of yellow crystals. It can be preserved in an atmosphere of carbon dioxide for weeks. On exposure to the atmosphere, it becomes viscid, and when light petroleum is added, a white insoluble oxidation product separates, which is also formed when a current of air is passed into the solution of the keten in benzene. Diphenylketen is vigorously acted on by water with the formation of diphenylacetic acid in quantitative yield. With ethyl alcohol, it forms ethyl diphenylacetate. It bears a further resemblance to carbimides in being acted on by primary bases, the *anilide* melting at 180°. The *amide* melts at 165° and the *phenylhydrazide* at 166–167°.

When a current of dry hydrogen chloride is passed into a solution of diphenylketen in benzene, diphenylacetyl chloride, boiling at 170–171° under 16 mm. pressure and melting at 55°, is obtained. When hydrogen chloride, containing traces of water, is passed into an ethereal solution of diphenylketen containing zinc chloride, ethyl diphenylacetate is formed.

The keten is much more stable towards water in benzene solution than in ethereal solution. When a benzene solution of the keten is agitated with dilute hydrochloric acid, *diphenylacetic anhydride* is formed. It boils at 220–225° under 15 mm. pressure and separates from ether in needles which melt at 98°.

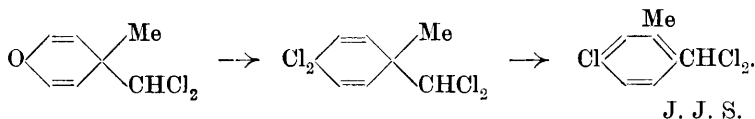
The unsaturated character of diphenylketen is further indicated by its power of combining with bromine, hydrogen sulphide, and ethyl sodiomalonate.

Phenylchloroacetyl chloride in ethereal solution was acted on by zinc dust. Phenylketen was not isolated from this reaction, but its existence was proved by the formation of phenylacetic acid on the addition of water.

A. McK.

Cyclic Ketones from Chloroform and Phenols. KARL AUWERS and GUSTAV KEIL (*Ber.*, 1905, **38**, 1693—1697. Compare Abstr., 1902, i, 218; 1903, i, 100, 620; 1904, i, 26).—When 4-keto-1-methyl-1-dichloromethyldihydrobenzene (Abstr., 1902, i, 218) is dissolved in light petroleum and mixed with an equivalent of phosphorus pentachloride at the ordinary temperature and the petroleum and oxychloride removed under reduced pressure, a chlorinated product is obtained which, on reduction with sodium and boiling alcohol, yields *o*-xylene. When the crude chlorinated product is heated with water at 160—180°, all the chlorine is removed from the side chain and *p*-chloro-*o*-tolualdehyde, $C_6H_4MeCl \cdot CHO$, is formed. It distils at 228°, has a sp. gr. 1.277 at 17°/17°, and solidifies to colourless crystals. Its *semicarbazone* crystallises in colourless needles and melts at 224°. On oxidation, the aldehyde yields Claus' *p*-chloro-*o*-toluic acid melting at 169—170° (Claus gives 172°).

The action of the pentachloride may thus be represented :



Intramolecular Atomic Migrations. III. Benzopinacones. P. J. MONTAGNE (*Rec. Trav. chim.*, 1905, **24**, 105—131).—The principal results recorded in this paper have already been published (Abstr., 1902, i, 472, and this vol., i, 58). Linnemann's method (*Annalen*, 1865, **133**, 6) was employed for the reduction of 4:4'-dichlorobenzophenone to dichlorodiphenylcarbinol; the *acetyl* derivative of the latter melts at 43.5°. 4:4':4'':4'''-Tetrachlorobenzopinacone, prepared from dichlorobenzophenone by Ciamician and Silber's method (Abstr., 1901, i, 36), forms molecular combinations with methyl alcohol (2 mols.), benzene (1 mol.), and toluene (1 mol.), melts at 147.5°, and decomposes at the same time into dichlorodiphenylcarbinol and dichlorobenzophenone; boiling with acetic acid induces the same decomposition.

4:4':4'':4'''-Tetrachlorobenzopinacolin, prepared from the foregoing by Zagumenny's method (Abstr., 1877, i, 459; 1881, 813), melts at 194°, and on boiling with alcoholic potassium hydroxide yields tri-*p*-chlorophenylmethane and *p*-chlorobenzoic acid. The former melts at 92° and crystallises from light petroleum in short, thick, transparent, rhombic prisms [$a:b:c=0.5904:1:0.9261$], which soon become opaque. The optical characters of the crystals were determined by Jaeger and are given in detail in the original.

Tri-*p*-nitrophenylcarbinol, when recrystallised from benzene, melts at 193° and does not combine with the solvent (compare Gomberg, Abstr., 1904, i, 490; E. and O. Fischer, *ibid.*, 864, and O. Fischer and Schmidt, *Zeit. Farb. Text. Ind.*, 1904, **3**, 1). The crystals are monoclinic prisms [$a:b:c=1.4825:1:2.9474$; $\beta=54^\circ 12'$]. Tri-*p*-aminophenylmethane melts at 202.5° (Graebe, 180°, Bernthsen, 203°, and E. Fischer, 207°). The trichlorophenylmethane, prepared from this by diazotisation in presence of cuprous chloride, is identical with that prepared from tetrachlorobenzopinacolin.

T. A. H.

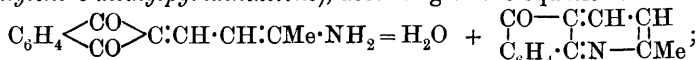
Derivatives of Indandione. GIORGIO ERRERA and E. CASARDI (*Gazzetta*, 1905, 35, i, 1—11. Compare Abstr., 1903, i, 265).—

Ethyl indandionemethenylacetoacetate, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} > CH \cdot CH : CAc \cdot CO_2Et$, formed by the condensation of indandione (1 mol.) with ethyl ethoxy-methyleneacetoacetate (1 mol.) in presence of sodium carbonate, separates from benzene or a mixture of benzene and light petroleum in yellow needles, turning red in the air and melting at 117—118°; it is an unstable compound and dissolves readily in bases, yielding the corresponding salts, or in alcohol. With aqueous ammonia, it yields aminomethyleneindandione, whilst on heating with ammonium acetate and acetic acid it gives α -di-*o*-benzylenonepyridine.

Indandionemethenylacetone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} > CH \cdot CH : CHAc$, formed by boiling ethyl indandionemethenylacetoacetate with dilute alkali hydroxide solution and subsequently acidifying, crystallises from ethyl acetate in golden-yellow needles melting at 177—178° and dissolving slightly in the ordinary solvents; with bases, it yields red, crystalline salts. The mother liquor from the indandionemethenylacetone contains methenylbisindandione and another compound separating from acetic acid in golden-yellow needles melting at 267.5°.

The *anhydride of indandionemethenylacetonedioxime*, $OH \cdot N : C \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} C : CH \cdot CH \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} CM_e$ or $OH \cdot N : C \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} C : CH : CH \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} CM_e$, prepared by boiling indandionemethenylacetone with excess of hydroxylamine hydrochloride in aqueous alcoholic solution, separates with $1H_2O$ from aqueous alcohol in yellow leaflets which melt and decompose at 246° and dissolve in solutions of bases.

The solution of indandionemethenylacetone in aqueous ammonia deposits brown or red crystals, $C_{13}H_{11}O_2N \cdot 2H_2O$, which melt and decompose at 240°, dissolve slightly in acetone and, when boiled with alkalis, yield ammonia and the original ketone. When boiled with concentrated acetic acid, this ammonia-derivative loses water and undergoes condensation, yielding 2-*o*-benzylenone-6-methylpyridine (2-phenylene-6-methylpyridineketone), according to the equation:



this compound crystallises from light petroleum in leaflets or flattened needles which melt at 121° and dissolve readily in alcohol or benzene. It is a feeble base, being precipitated from acetic acid solution by water; the *hydrochloride* crystallises in slender, yellow needles, slightly soluble in concentrated hydrochloric acid. It yields an *oxime*, $C_{13}H_{10}ON_2$, crystallising from alcohol in minute, yellowish-white scales, which melt at 256—257° and dissolve slightly in light petroleum and readily in xylene.

2-*o*-Benzylene-6-methylpyridine, $\begin{smallmatrix} CH_2 - C : CH \cdot CH \\ | \quad | \quad | \\ C_6H_4 \cdot C : N - CM_e \end{smallmatrix}$, obtained by reducing the corresponding ketone by means of hydriodic acid and phosphorus, is deposited as a *hydrate* (with $2H_2O$) in the form of shining, white needles which melt at 45—48° to a turbid liquid and at

100° to a clear liquid; the crystals lose their water of crystallisation in a vacuum over potassium hydroxide, yielding anhydrous, hexagonal crystals of the formula $C_{13}H_{11}N$, which have a faintly aromatic odour and melt at 31–32° and boil with slight decomposition at 325°. The *hydrochloride*, $C_{13}H_{11}N \cdot HCl$, crystallises in long, silvery needles, which melt at 282° and dissolve slightly in hydrochloric acid and moderately well in water. The *picrate*, $C_{13}H_{11}N \cdot C_6H_3O_7N_3$, crystallises from alcohol in yellow needles melting at 211–212°. T. H. P.

Amino-derivatives of Anthraquinone. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 156803).—When a cooled solution of α -diazoanthraquinone sulphate is oxidised by an excess of sodium hypochlorite, yellow needles of the *sodium salt of anthraquinone- α -nitroamine*, $C_{14}H_7O_2 \cdot NNa \cdot NO_2$, separate. When decomposed by dilute acids or carbon dioxide, the *nitroamine* is obtained, and crystallises from dilute acetic acid in yellow needles, melting and decomposing at 193°. It is insoluble in water, and dissolves sparingly in alcohol, acetone, or benzene. Fuming nitric acid converts it into *4-nitroanthraquinone- α -nitroamine*, a light brown, crystalline powder, exploding at 117°. Sodium sulphide reduces it to 1:4-diaminoanthraquinone.

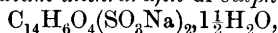
Anthraquinone-1:5-dinitroamine, $C_{14}H_6O_2(NH \cdot NO_2)_2$, prepared in similar manner, explodes at 203° and forms a golden-yellow *sodium salt*. Nitric acid converts it into *4:8-dinitroanthraquinone-1:5-dinitroamine*, which explodes at 134°. Sodium sulphide reduces it to 1:4:5:8-tetra-aminoanthraquinone, characterised by the blue colour of its acetone solution. C. H. D.

Connection between the Constitution and the Colour and Dyeing Power with Mordants of the Hydroxyanthraquinones and their Sulphonic Acids. GEORG VON GEORGIEVICS (*Zeit. Farb. Text. Ind.*, 1905, 4, 185–192. Compare Möhlau and Steimmig, *ibid.*, 3, 273 and 358).—The fact that 3-hydroxyanthraquinone is a strong mordant dye is regarded as indicating the incompleteness of Möhlau and Steimmig's view that tinctorial properties in the anthraquinone series are produced by a hydroxyl group in the ortho-position. A simple rule connecting the dyeing properties and the constitution of these substances cannot be deduced. A hydroxyl group in position 3 in alizarin produces a far greater effect than the same group introduced into any other position in the molecule; anthragallol (1:2:3-trihydroxyanthraquinone) dyes brown shades, which may be regarded as produced by a combination of 1:3- and 2:3-dihydroxyanthraquinones. All other hydroxylated alizarins resemble the parent substance in giving red dyes. The influence on the colour of a hydroxyl group in position 5 or 8 is greater than that of the same group in position 6 or 7; moreover, the effect when in position 5 is greater than when in position 8. A hydroxyl group introduced into position 5 in quinizarin (1:4-dihydroxyanthraquinone), instead of increasing the dyeing power towards mordanted fabrics, diminishes it; the product behaves as a combination of 1:8- and 1:5-dihydroxyanthraquinones, these two substances possessing little tinctorial

properties towards mordants. Probably for a similar reason, 1:4:5:8-tetrahydroxyanthraquinone has little tinctorial value.

On sulphonation with sulphuric acid containing 20 per cent. of anhydride, dihydroxyanthraquinones containing both hydroxyl groups in the same nucleus give monosulphonic acids; when the two hydroxyls are heteronuclear, a disulphonic acid is obtained. The entrance of the sulphonic group, in all the cases studied, caused an intensification of the dyeing properties towards mordants.

Sodium quinizarinsulphonate, $C_{14}H_7O_4 \cdot SO_3Na, 2\frac{1}{2}H_2O$, crystallises in spherular aggregates of very slender needles or in thin plates. *Sodium xanthopurpurinsulphonate*, with $\frac{3}{2}H_2O$, forms hard, brown needles. *Sodium 1-hydroxyanthraquinonesulphonate* forms golden-yellow needles, and probably contains $1H_2O$; the isomeric *sodium 2-hydroxyanthraquinonesulphonate* crystallises from dilute alcohol in sheaves of needles containing $1H_2O$. *Sodium anthrarufin-di-sulphonate*,



forms microscopic, prismatic crystals. The *sodium* salt of sulphoanthraflavic acid, $C_{14}H_6O_4(SO_3Na)_2$, seems to contain $3H_2O$.

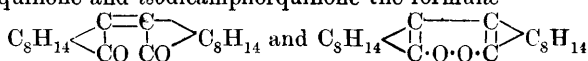
W. A. D.

Action of Acetic Anhydride and Sodium Acetate on Phenanthraquinone. WASSILI SCHARWIN (*Ber.*, 1905, 38, 1270—1272).—When heated on a water-bath with sodium acetate and acetic anhydride, phenanthraquinone yields, as the principal product of the reaction, a *substance*, $C_{33}H_{22}O_7$, which crystallises in colourless, transparent, rhombic plates, becomes dark blue, and decomposes at about 250° ; becomes yellow when exposed to light, and dissolves in concentrated sulphuric acid to an olive-green solution. When warmed with aqueous sodium hydroxide, it is converted into Meyer and Spengler's lactone, $C_{16}H_8O_8$ (this vol., i, 219). The action of phenylhydrazine on the substance $C_{33}H_{22}O_7$ leads to the formation of a *compound*, $C_{18}H_{12}O_3$, which crystallises in orange needles, melts and decomposes at 251° , and dissolves in concentrated sulphuric acid to a violet solution.

Along with the main product, phenanthraquinone yields small quantities of diacetylphenanthraquinol and of a *substance* which crystallises in opaque, glistening, bronze rhombohedra and dissolves in benzene, chloroform, or concentrated sulphuric acid to blue solutions, which become colourless when exposed to light.

G. Y.

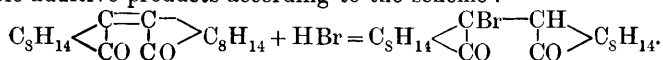
Dicamphorquinone and isoDicamphorquinone. GIUSEPPE ODDO (*Gazzetta*, 1905, 35, i, 12—27).—On the basis of Komppa's synthesis of camphor according to Bredt's formula, the author attributes to dicamphor the structural formula $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{CO} \quad \text{CO} \end{smallmatrix} C_8H_{14}$, and to dicamphorquinone and isodicamphorquinone the formulæ



respectively.

Dicamphorquinone is partially or completely converted into the

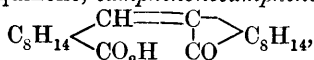
isomeric isodicamphorquinone by the action of hydrobromic acid, bromine, nitrosyl chloride, potassium permanganate, chromium trioxide, sodium peroxide, phosphorus pentachloride, nitrobenzene, or concentrated potassium hydroxide solution or by fusion with potassium hydroxide. The isodicamphorquinone formed either remains unchanged or is but slightly attacked by the reagents named. In the above isomerisation, the author assumes the formation of intermediate unstable additive products according to the scheme :



The latter then splits up, giving either the original dicamphorquinone or its isomeride.

Only one such *additive compound*, $\text{C}_8\text{H}_{14} \left\langle \begin{array}{c} \text{Cl}-\text{C}(\text{OH}) \\ \text{CO} \quad \text{CO} \end{array} \right\rangle \text{C}_8\text{H}_{14}$, was obtained, and was prepared by the action of yellow mercuric oxide (2 mols.) and iodine (2 mols.) on dicamphorquinone (1 mol.) in alcohol. It crystallises from benzene in small, dark red, shining scales melting at 142—145°, and is converted into dicamphorquinone by aqueous sulphurous acid, and into camphorquinone by boiling its alcoholic solution with yellow mercuric oxide until decolorised.

Fusion of dicamphorquinone with potassium hydroxide yields, besides isodicamphorquinone, *camphenonecamphenoic acid*,



which is also obtained in small quantity when isodicamphorquinone is fused with potassium hydroxide.

When boiled for a long time with nitric acid, dicamphorquinone is converted into camphoric anhydride and camphoric acid, whilst under the same conditions isodicamphorquinone is almost completely changed, but yields no definite products.

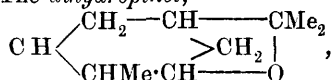
The action of sodium or magnesium on $\beta\beta$ -dibromocamphor in toluene solution yields dicamphor, resinous substances, and dicamphorquinone. In ethereal solution, magnesium and $\beta\beta$ -dibromocamphor give the compound $\text{C}_8\text{H}_{14} \left\langle \begin{array}{c} \text{CBr}\cdot\text{MgBr} \\ \text{CO} \end{array} \right\rangle \frac{1}{2}\text{Et}_2\text{O}$. T. H. P.

Carvone. HANS RUPE and PAUL SCHLOCHOFF (*Ber.*, 1905, **38**, 1719—1725).—A 55 per cent. yield of 8-hydroxy-8 : 9-dihydrocarvone, $\text{CMe} \left\langle \begin{array}{c} \text{CH}\cdot\text{CH}_2 \\ \text{CO}-\text{CH}_2 \end{array} \right\rangle \text{CH}\cdot\text{CMe}_2\cdot\text{OH}$, is obtained when carvone is shaken for 70 hours with 10 times its weight of 40 per cent. sulphuric acid. It distils at 154° under 10 mm. pressure, solidifies on cooling, and melts at 41—42°. It is readily soluble in water and organic solvents, has a sp. gr. 0.8282 at 20° and $[\alpha]_D + 43.06^\circ$ at 20°. The *oxime*, $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$, crystallises in colourless needles melting at 114—114.5° and sparingly soluble in water. The *semicarbazone*, $\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}_3$, crystallises from dilute alcohol in flat needles and melts at 176°. When reduced, the dihydrocarvone yields 2 : 8-dihydroxyterpane, which is identical with Baeyer's glycol (*Abstr.*, 1895, i, 550) melting at 112—113°.

When dihydrocarveol is shaken with 35 per cent. sulphuric acid

during 48 hours, the product is a mixture of Baeyer's glycol, α -2:8-dihydroxyterpane, and a stereoisomeride, β -2:8-dihydroxyterpane. A better yield of the latter is obtained by shaking with 40 per cent. acid during 90 hours. It is less soluble in benzene than the α -compound, crystallises in slender, colourless needles, melts at 103—104°, and combines with sulphuric acid more readily than the stereoisomeride. Its sp. gr. is 0.8273 at 20° and it has $[\alpha]_D + 12.61^\circ$ at 20°.

When an acetone solution of the crude dihydroxyterpane is slowly added to boiling 25 per cent. sulphuric acid through which steam is being passed, a mixture of dihydropinol, terpenes, dihydrocarveol, and cymene is obtained. The *dihydropinol*,



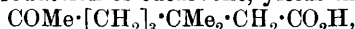
is most readily isolated as its *ferricyanide*, which is then decomposed by sodium carbonate. The oxide distils at 58.5° under 9 mm. pressure, has a sp. gr. 0.9192 at 20° and $[\alpha]_D + 34.97^\circ$ at 20°, and closely resembles cineol. J. J. S.

Terpenes and Ethereal Oils. Constitution of Eucarvone and its Reduction Products. OTTO WALLACH [with HUGO KÖHLER]

(*Annalen*, 1905, 339, 94—116).—The formula $\begin{matrix} \text{CMe} \cdot \text{CO} \cdot \text{CH} \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \end{matrix} > \text{CMe}_2$,

proposed by Baeyer for eucarvone, is not in accord with many of the reactions discovered by that investigator, and still less with other recent observations.

By reducing eucarvone, Baeyer only obtained the unsaturated dihydroeucarveol, $\text{C}_{10}\text{H}_{17} \cdot \text{OH}$, but it has been found that at the same time 14—20 per cent. of the saturated tetrahydroeucarveol, $\text{C}_{10}\text{H}_{19} \cdot \text{OH}$, is also formed. Further, pure eucarvoxime yields tetrahydroeucarylamine, together with the saturated ketone, $\text{C}_{10}\text{H}_{18}\text{O}$, as by-product. Baeyer has shown that the tetrahydrocarvone has a seven-membered ring, $\begin{matrix} \text{CHMe} \cdot \text{CO} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{CH}_2 \end{matrix} > \text{CMe}_2$, and, further, the saturated ketone, $\text{C}_{10}\text{H}_{18}\text{O}$, obtained by direct reduction of eucarvone, yields the *keto-acid*,



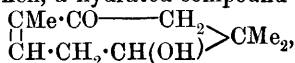
which can be converted into $\beta\beta$ -dimethylpimelic acid,



the latter giving 1:1'-dimethylcyclo-3-hexanone, $\begin{matrix} \text{CH}_2 \cdot \text{CO} - \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \end{matrix}$.

These facts suggest that eucarvone has a seven-membered ring, $\begin{matrix} \text{CMe} \cdot \text{CO} \cdot \text{CH}_2 \\ | \\ \text{CH} - \text{CH} \cdot \text{CH} \end{matrix} > \text{CMe}_2$. The oxamino-oxime of eucarvone yields, on reduction, an unsaturated diamine of which the phosphate on distillation gives not *m*-cymene, but *p*-cymene.

In the formation of eucarvone from the hydrobromide of carvone, it is suggested that under the influence of the alkali hydroxide the three-membered ring is broken, a hydrated compound being formed,



which then passes into eucarvone. It is uncertain what position the ethylene linking occupies in dihydroeucarvone; it is possible that in the reduction a rearrangement has taken place.

Eucarvone is prepared from carvone hydrobromide and methyl alcoholic potassium hydroxide, and purified by conversion into the semicarbazone; it boils at 85–87° under 12 mm. pressure, has a sp. gr. 0.949 and $n_D = 1.5092$ at 21°, and is optically inactive. When reduced in absolute alcohol in moist ether, a mixture of dihydroeucarvone and an alcohol are obtained, which is oxidised with 10 per cent. potassium permanganate, the alcohol remaining unchanged. Tetrahydroeucarvone is prepared by oxidising the alcohol with chromic acid; it boils at 91–93° under 13 mm. and at 212–216° under the ordinary pressure, and has a sp. gr. 0.918 and $n_D = 1.4673$ at 22°; its oxime is a liquid, and its semicarbazone consists of a mixture of two compounds differing in solubility and melting at 161–163° and 191–192° respectively. On oxidation with chromic acid in the presence of sulphuric acid, it yields a keto-acid, which is a liquid solidifying in a freezing mixture and boiling at 194–196° under 39 mm. pressure; its *semicarbazone* melts at 170–171° and its *oxime* at 100–101°. When treated with sodium hypobromite, $\beta\beta$ -dimethyl-pimelic acid, melting at 102–103°, is obtained; its calcium salt, on distillation with soda lime, yields 1:1'-dimethyl-3-cyclohexanone, which melts at 173–175° and gives a *semicarbazone* sintering at 192° and melting at 195°.

Tetrahydrocarveol is prepared by reducing the pure tetrahydroeucarvone, boils at 219–220°, and yields, with phenylcarbimide, a *phenylurethane* melting at 74–75°.

Tetrahydrocarvone can be converted into a ketonic acid and then into isopropyladipic acid (m. p. 75–76°), in the same manner as tetrahydroeucarvone.

Eucarvoxime yields a hygroscopic *hydrochloride*, $C_{10}H_{14} \cdot NOH, HCl$, which is a snow-white powder melting at 68–70°; a hydrobromide melting and decomposing at 77–79°, and a hydriodide were also prepared. On reducing an alcoholic solution of the oxime by sodium, tetrahydroeucarvylamine is obtained; it is an oil boiling at 209–211°; its *benzoyl* derivative melts at 168°.

K. J. P. O.

Ethereal Oil of Birch Buds. HUGO VON SODEN and FRITZ ELZE (*Ber.*, 1905, 38, 1636–1638).—The essential oil of birch buds contains:

(1) A paraffin, which separates from methyl alcohol in odourless, tasteless needles melting at 50°, and is readily soluble in ether, benzene, or light petroleum. (2) An ester not yet investigated. (3) A primary sesquiterpene alcohol, $C_{15}H_{23} \cdot OH$, to which the name *betulol* is given. It is a colourless, very viscous oil, with an odour resembling that of incense and a bitter taste. It has a sp. gr. 0.975 at 15°, $[\alpha]_D - 35^\circ$, and boils at 138–140° under 4 mm., and, with partial decomposition, at 284–288° under 743 mm. pressure. It is soluble in 3 parts of 70 per cent. alcohol. *Betulol acetate*, $CH_3 \cdot CO_2 \cdot C_{15}H_{23}$, is a colourless, faintly aromatic smelling oil, which has the sp. gr. 0.986 at 15° and boils at

142—144° under 4 mm. pressure. The acid phthalate is obtained as a transparent resin showing no tendency to crystallise. T. H. P.

Gutta-percha from German New Guinea. ALEXANDER TSCHIRCH and O. MÜLLER (*Arch. Pharm.*, 1905, **243**, 114—132. Compare Abstr., 1904, i, 76).—The sample examined was the product of *Palaequium supfianum*; the percentage of it soluble in water, alcohol, acetone, alcohol-chloroform, ether, and light petroleum respectively was 1, 12, 15, 34, 40, 40 at 17°, 2, 40, 42, 50, 96, 97 at the boiling temperature, whilst in benzene, toluene, chloroform, and carbon bisulphide 97 per cent. dissolved at both temperatures.

The material was extracted thoroughly with boiling water, then with boiling 96 per cent. alcohol. From the alcoholic extracts, alban crystallised, but consisted of three different crystalline forms; these were separated by digestion with 96 per cent. alcohol, first at 40°, then at 60°, and crystallisation until fractions were obtained with a uniform appearance under the microscope. α -Guinalban (needle-alban), $C_{42}H_{70}O$, crystallises in needles and melts at 171°; β -guinalban (crystal-alban), $C_{22}H_{32}O$, crystallises in lustrous plates and melts at 136°; γ -guinalban (spherite-alban), $(C_{22}H_{32}O)_4$ (molecular weight determined), crystallises in little spheres and melts at 111°. β - and γ -Guinalbans both yield cinnamic acid when boiled with alcoholic potassium hydroxide (compare van Romburgh, Abstr., 1904, 905); in addition, they yielded respectively β -guinalbaresinol, melting at 107°, and γ -guinalbaresinol, $C_{26}H_{44}O$, melting at 168°, both of which crystallise in needles. The amount of α -guinalban did not permit of a similar experiment being made with it; nor did the amount of β -guinalbaresinol permit of an analysis.

The mother liquor from the guinalban was poured into water acidified with hydrochloric acid, when guinafluavil was precipitated; by treatment with 80 per cent. alcohol, it was separated into an insoluble, α , and a soluble, β , portion, both yellow and amorphous. α -Guinafluavil, $(C_{22}H_{36}O)_3$ (molecular weight determined), melts at 83°; β -guinafluavil, $C_{15}H_{24}O$, at 78°; both yield cinnamic acid when boiled with alcoholic potassium hydroxide, and in addition respectively α -guinafluaviloresinol, $C_{25}H_{48}O_2$, which melts at 136°, and β -guinafluaviloresinol, which melts at 143°; these crystallise best from acetone. From some crude fluavil, a product was obtained by hydrolysis which separated from a solution in dilute alcohol, on slow evaporation of the solvent, in forms resembling in structure grains of potato starch; after crystallisation from acetone, it melted at 172°, and had the composition $C_{28}H_{48}O_2$.

The residue left after the extraction of the gutta-percha with alcohol was dissolved in chloroform and the solution was poured into alcohol; the precipitated albanan was crystallised from alcohol-chloroform. Guinalbanan, $C_{48}H_{88}O$, melts at 62° and takes up oxygen gradually from the air, especially when exposed to light.

The substance remaining in solution when the albanan was precipitated was purified by repeated solution in chloroform and precipitation with alcohol. This substance, *guinagutta*, $C_{10}H_{16}$, separates from a hot ethereal solution, on cooling, as an apparently amorphous, white

mass, which under the microscope is seen to contain curved needles ; at 60°, it shrinks to a glassy mass ; alcoholic potassium hydroxide does not act on it ; when exposed to the air it turns red.

The colour reactions of a number of these substances are tabulated and compared with those of phytosterol, which they resemble in many respects.

In all, 500 grams of the gutta-percha were worked up. From 300 grams, the yield of crude alban was 86 grams, of crude fluavil 25 grams. The weights of pure alban obtained were α , 0.3 ; β , 2.5 ; γ , 10.0 grams ; of albanan, about 2 grams.

It will be noticed that the terms alban, fluavil, albanan, and gutta are used as generic names, a syllable being prefixed to them to indicate the material from which particular varieties of them are derived. When several substances have the same name, that distinguished as α has the highest melting point, that called β the next highest, &c.

C. F. B.

The Albans and Fluavil of Sumatra Gutta-percha. ALEXANDER TSCHIRCH and O. MÜLLER (*Arch. Pharm.*, 1905, 243, 133—140. Compare Abstr., 1904, i, 76, and preceding abstract for the nomenclature). — α -Sumalban (crystal-alban), from old gutta-percha, is hydrolysed by 10 per cent. alcoholic potassium hydroxide to cinnamic acid and crystalline α -sumalbaresinol, $C_{52}H_{84}O_2$ or $C_{50}H_{80}O_2$, which melts at 207°. β -Sumalban (spherite-alban), from old gutta-percha and from a commercial sample, yields cinnamic acid and crystalline β -sumalbaresinol, $C_{50}H_{80}O_2$ or $C_{48}H_{76}O_2$ (molecular weight determined), which melts at 151°. γ -Sumalban (isospherite-alban), from commercial gutta-percha, yields cinnamic acid and crystalline γ -sumalbaresinol, $C_{40}H_{64}O_2$, which melts at 171°.

Fluavil from old gutta-percha yields cinnamic acid when hydrolysed with alcoholic potassium hydroxide, but the resinol also formed could not be made to crystallise either from acetone or from dilute alcohol. Fluavil from commercial gutta-percha is not decomposed.

Sumagutta, both from old and from commercial gutta-percha, is not attacked by alcoholic potassium hydroxide.

The colour reactions of these substances were compared with those of phytosterol, and are tabulated in the paper. C. F. B.

Albans of Mikindani-caoutchouc from German East Africa. ALEXANDER TSCHIRCH and O. MÜLLER (*Arch. Pharm.*, 1905, 243, 141—146).—The variety of india-rubber from Mikindani in German East Africa, known as Mozambique Balls, contains a certain amount of resin, and this was investigated for comparison with the resins of gutta-percha. The sample was boiled with water and then extracted thoroughly with acetone. From the solution, a crude alban crystallised ; the mother liquor, when evaporated, left a yellow, sticky mass easily soluble in cold alcohol, with a few crystals of the alban, of which 3.5 grams in all were obtained from 1000 of the rubber. The crude material melted at 168—172°, and was seen under the microscope to consist of two substances ; it was separated into these by treatment

with 96 per cent. alcohol at 60°. Of the more soluble portion, *α-danialban*, $C_6H_{12}O$, 0.9 gram was obtained; it crystallises in spherites, melts at 178°, and is not stable in the air. The yield of the less soluble portion, *β-danialban*, $C_{30}H_{48}O$, was 1 gram; it crystallises in plates and melts at 149°. Neither of these substances yields cinnamic acid when heated with alcoholic potassium hydroxide, differing in this respect from the albanes obtained from gutta-percha.

Several colour reactions of these substances are tabulated; in these, the substances much resemble phytosterol. C. F. B.

A White Peru Balsam. [C. HARTWICH and] A. HELLSTRÖM (*Arch. Pharm.*, 1905, 243, 218–237. Compare Thoms and Biltz, *Abstr.*, 1904, i, 1038).—The sample examined came from Honduras, and was a cloudy, yellow, syrupy liquid having a sp. gr. 1.089, $n_D + 7.20'$, n_D 1.5925 at 20°, acid number 27, saponification number 165; 94 per cent. of it dissolved in alcohol, and it contained 75 per cent. of cinnamein (aromatic esters).

The portion insoluble in alcohol consisted of *honduresen*, $C_{64}H_{64}O_{10}$, a white, amorphous substance which melts at 310–315° and is very inert chemically, but is decomposed by fusion with potassium hydroxide with formation of benzoic acid and a brown resin.

The alcoholic solution of the balsam was evaporated, and the residue dissolved in ether. When the ethereal solution was shaken with 5 per cent. aqueous sodium carbonate, a sticky substance separated which crystallises from alcohol; this is a sodium derivative of *honduresinol*, $C_{16}H_{26}O_2$, which itself is amorphous, melts at 286°, gives colour reactions resembling those of cholesterol, and in general much resembles benzoiresinol and storesinol (Tschirch, *Abstr.*, 1893, i, 480; 1902, i, 109). The sodium carbonate solution was found to have taken up much cinnamic acid.

The ethereal solution was then extracted with 1 per cent. aqueous potassium hydroxide. By salting out the extract with concentrated aqueous sodium hydroxide, a product was obtained which can be crystallised from alcohol; this is the salt of a substance, itself amorphous, which melts at 156–161°, has the composition $C_{16}H_{26}O_2$, and appears to be identical with styresinol (Tschirch, *Abstr.*, 1902, i, 110). A little more of this is precipitated when the alkaline solution is acidified, together with much cinnamic acid and *honduresinotannol*, $C_{40}H_{45}O_{10}$, which is brown and amorphous, begins to shrink together at 300°, forms an amorphous *acetyl* derivative melting at 215°, and in its reactions resembles siarresinotannol (Ludy, *Abstr.*, 1893, i, 666).

The ethereal solution was then shaken with aqueous sodium hydrogen sulphite, but no aldehyde or ketone could be isolated.

The ethereal solution now remaining was evaporated and the residue distilled with steam. The non-volatile portion was hydrolysed with concentrated sodium hydroxide solution; the products were cinnamic alcohol, phenylpropyl alcohol, cinnamic acid, and a little styresinol. The volatile portion consisted of phenylpropyl alcohol and a *terpene*, $C_{10}H_{16}$, which boiled at 261–262° and took up 2 atoms of bromine in acetic acid solution. C. F. B.

Solanin from *Solanum sodomæum*. GIUSEPPE ODDO and AMEDEO COLOMBANO (*Gazzetta*, 1905, 35, i, 27—45).—The widely varying data given by different authors concerning solanin are probably to be explained by the fact that the various solanins obtained from different sources are not one and the same product. It is also possible that, at different stages of their growth, the plants contain compounds of analogous behaviour, but different compositions.

The authors have used various methods for the extraction of solanin from *Solanum sodomæum*, the most convenient consisting of prolonged maceration (5 months) with 91 per cent. alcohol, the filtered extract being then treated with 1 per cent. acetic acid solution and subsequently with lime-water; on boiling the precipitate thus obtained with 80 per cent. alcohol in a current of carbon dioxide, a yield of 0.266 per cent. of solanin is obtained. Its composition is $2C_{23}H_{39}O_8N, H_2O$, the water being lost on drying at 105° , and it crystallises from 80 per cent. alcohol in flocculent aggregates of slender, white needles, which turn brown at 230° and melt and decompose at 245 — 250° , and when powdered form microscopic, transparent scales. It is very slightly soluble in absolute alcohol, and gelatinises in 90 per cent. alcohol; it dissolves slightly in acetone, and more so in methyl alcohol, which deposits crystals melting at 275 — 280° . Its principal reactions are as follows: when a small quantity is treated with a drop of cold concentrated sulphuric acid, it becomes first yellow and then deep red, afterwards slowly changing to violet and brown; the coloration is more intense with the product crystallised from methyl alcohol. The solution in concentrated nitric acid is colourless at first, but changes to pale yellow, which deepens after a time. A drop of a hot mixture of absolute alcohol and sulphuric acid does not impart the green colour to the crystals described by Cazeneuve and Breteau (*Abstr.*, 1899, i, 551), but after a time the liquid assumes a pale rose-red colour; with this same reagent, a sample of solanin from commercial *Solanum tuberosum* gave a pale violet coloration, the liquid becoming rose-red. With the double iodide of bismuth and potassium, it gives a dark yellow precipitate, becoming paler on standing. Phosphomolybdic acid gives a greenish-white precipitate, and the Froehde-Buckingham reagent yields first a yellow coloration which reddens and turns brown after a few minutes. The best reaction is that of Missaggi (*Gazzetta*, 1875, 5, 417), which is, however, also given by solanidin. It consists in adding one or two drops of dilute platinic chloride solution to a few drops of solanine solution in a watch-glass, and evaporating on a water-bath at 65 — 70° until almost dry; a red coloration then appears, which changes to intense purple and becomes violet if the heating is continued; the colour slowly disappears if the heating is stopped, but it returns when the glass is again put on the bath. If an alcoholic solution of solanin is slowly evaporated on a water-bath with a solution of platinic iodide and potassium iodide, a yellow coloration appears which becomes red and finally violet with green layers, more especially when cold.

Solanin hydrochloride, $C_{23}H_{39}O_8N, HCl$, separates from a mixture of alcohol and ether in shining, microscopic scales which begin to blacken at about 135° , do not melt at 265° , and are soluble in water. The

aureichloride forms a yellow, crystalline precipitate which is soluble in alcohol, begins to blacken at 115° and decomposes at 122° . The *platinichloride* forms a crystalline powder somewhat soluble in water.

Solanin evidently contains an amino-group in the aromatic nucleus, since with nitrous acid and β -naphthol it apparently becomes converted into an oxyazo-compound, which functions as an indicator, being turned red by acids and yellow by alkalis.

When boiled with 2 per cent. hydrochloric acid, solanin undergoes hydrolysis to solanidin, $C_{19}H_{29}ON$, which crystallises from aqueous alcohol in small, nacreous scales melting at 190 – 192° , and dissolves in ether and, to a slight extent, in acetone or light petroleum. Its alcoholic solution has a faintly alkaline reaction, and it forms difficultly soluble salts. It can be diazotised and with β -naphthol gives a product which behaves towards acids and alkalis similarly to the corresponding product obtained from solanin. Besides solanidin, the hydrolysis of solanin by hydrochloric acid yields a dextrorotatory hexose, giving an osazone, $C_{18}H_{22}O_4N_4$, which melts and decomposes at 186° .
T. H. P.

Solanin. JOHANN WITTMANN (*Monatsh.*, 1905, 26, 445–467. Compare Firbas, Abstr., 1890, 75; Schulz, Abstr., 1901, i, 92; Hilger and Merckens, Abstr., 1903, i, 847; Zeisel and Wittmann, Abstr., 1904, i, 80; Votoček and Vondráček, Abstr., 1904, i, 177).—Firbas' formulæ for solanin, $C_{52}H_{93}O_{18}N$, and for solanidin, $C_{40}H_{61}O_2N$, are confirmed by analysis, and, for the latter, by molecular weight determinations by the boiling point method. The sugar obtained by hydrolysis of solanin contains galactose, rhamnose, and a sugar or mixture of sugars which has $[\alpha]_D + 33.65^{\circ}$, yields an osazone which melts at 198 – 200° , and is probably a polysaccharide. The presence of dextrose could not be determined with certainty.
G. Y.

Caryophyllin. HANS MEYER and OTTO HÖNIGSCHMID (*Monatsh.*, 1905, 26, 379–389).—Caryophyllin is obtained from the buds of *Caryophyllus aromaticus* by digestion with alcohol at the laboratory temperature for 14 days, or by extraction with ether and removal of resinous impurities by treatment of the product with aqueous sodium hydroxide or ammonia. It crystallises from alcohol in clusters of long, slender, silky needles, melts at 295° , sublimes without decomposition in a vacuum, is without odour or taste, and gives Liebermann's cholesterol reaction. The *tetra-acetyl* derivative, $C_{40}H_{60}O_4Ac_4$, crystallises in slender, colourless needles, commences to soften at 245° , and melts at 268 – 271° . Caryophyllic acid, $C_{40}H_{64}O_{12}$ or $C_{40}H_{62}O_{12}$, formed by treatment of caryophyllin with fuming nitric acid (compare Mylius, *Ber.*, 1873, 6, 1053), crystallises in colourless needles, which become red on exposure to direct sunlight, and forms amorphous, yellow salts. The *methyl* ester, $C_{40}H_{60}O_8(OMe)_4$, formed by the action of diazomethane on the acid in ethereal solution, or of methyl iodide on the silver salt, crystallises in slender, colourless needles and melts at 164 – 165° . When boiled with sodium acetate and acetic anhydride, the acid forms an *acetyl* derivative, which crystallises in slender, colourless needles, melts at 200 – 204° , and decomposes at 206° .

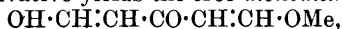
The action of diazomethane on caryophyllin leads to the formation of the *methyl ether*, $C_{40}H_{63}O_8 \cdot OMe$, which melts at 187° and forms a *triacetyl derivative*, $OMe \cdot C_{40}H_{60}(OAc)_3$. This crystallises in broad, glistening needles and melts at $212-213^\circ$. G. Y.

Influence of Active Groups in the Textile Fibres on the Process of Dyeing. WILHELM SUIDA (*Monatsh.*, 1905, 26, 413—427. Compare this vol., i, 75).—The action of acylating or of alkylating reagents on cotton-wool produces no change in its behaviour towards pararosaniline, crystal-violet, bordeaux extra, or azopararosaniline. When shaken with benzoyl chloride and aqueous sodium hydroxide, cotton-wool acts as a catalytic agent, accelerating the formation of benzoic acid and sodium chloride. Pararosaniline solution, after decolorisation with cotton-wool, gives a strong chlorine reaction, showing the salt to have been dissociated in the process of dyeing. It is probable that, owing to the slightly active nature of the hydroxyl groups in cellulose, the dyeing of cotton-wool is a physical process.

Wool and silk, which are aminocarboxylic acids, are dyed, in the neutral bath, an intense red by pararosaniline, intense violet by crystal-violet, and a weak red by azopararosaniline. After treatment with acetyl chloride, acetic anhydride, or absolute alcohol and sulphuric acid, wool and silk are only slightly coloured by pararosaniline or crystal-violet, but are dyed an intense red by azopararosaniline. The microscopic appearance of the wool or silk fibres is not altered by acetylation or alkylation; after hydrolysis with aqueous ammonium carbonate, the fibres give the same reaction as untreated wool or silk to the three dyes in question. Wool or silk fibres which have been treated with benzoyl chloride and aqueous sodium hydroxide are partially dyed, whilst fibres which have been boiled with ethyl bromide, which results probably in ethylation of the amino-, but not of the carboxyl-, groups, are dyed the normal colours. G. Y.

Pyrone. II. RICHARD WILLSTÄTTER and RUDOLF PUMMERER (*Ber.*, 1905, 38, 1461—1472. Compare *Abstr.*, 1904, i, 1043; *Collie, Trans.*, 1904, 85, 971).—When warmed for a short time with dilute alkalis, pyrone is transformed into derivatives of bishydroxymethyleneacetone, $CO(CH:CH \cdot OH)_2$. With aqueous potassium hydroxide, the dipotassium derivative is formed, and with potassium methoxide the methyl potassium derivative, $OK \cdot CH:CH \cdot CO \cdot CH:CH \cdot OMe$, which was previously described as an additive compound of pyrone and potassium methoxide. The monopotassium derivative, when heated with methyl iodide and methyl alcohol, yields the *dimethyl ether*, $CO(CH:CH \cdot OMe)_2$, in the form of an oil distilling at $138-142^\circ$ under $13.5-14$ mm. pressure. Its alcoholic solution is neutral, gives only a faint pink coloration with ferric chloride, and is soluble in water. Pyrone, 3-methylpyrone, and an *oil*, $C_8H_{14}O_3$, boiling at $75-81^\circ$ under 10 mm. or at $191-194^\circ$ (corr.) under atmospheric pressure are formed during the methylation.

The addition of an ethereal solution of hydrogen chloride to the monopotassium derivative yields the free *monomethyl ether*,



as a yellow oil with acid properties; it gives a deep red coloration with ferric chloride, and is readily transformed into pyrone. The potassium compound gives precipitates with silver nitrate, mercuric chloride, mercurous nitrate, and cupric chloride. The *cupric* salt, $(C_6H_7O_3)_2Cu$, crystallises from ethyl acetate in glistening, greyish-green prisms melting at 157–158°.

The *benzoate*, $OBz \cdot CH : CH \cdot CO \cdot CH : CH \cdot OH$, obtained by carefully hydrolysing the methyl benzoate (m. p. 98·5–99°) previously described, crystallises from light petroleum in yellow plates melting at 80·5–81°. It has an acid reaction, gives a coloration with ferric chloride, and is readily hydrolysed. When dissolved in sodium carbonate solution and immediately precipitated with sulphuric acid, a second modification is obtained. This also melts at 81°, but is less soluble in light petroleum and crystallises differently. The *copper* derivative, $(C_{12}H_9O_4)_2Cu$, crystallises in long, soft, green prisms and decomposes at 200°.

The *dibenzoate*, $CO(CH : CH \cdot OBz)_2$, obtained by shaking a solution of pyrone in sodium hydroxide with benzoyl chloride or by further benzoylating the monobenzoyl compound, separates from alcohol in colourless prisms, melts at 111·5–112°, and gives a red coloration with ferric chloride after a time or on heating. An alcoholic solution of pyrone containing hydrogen chloride readily reacts with ethyl orthoformate, even at the ordinary temperature, yielding the *hexaethylacetal* of diformylacetone, $C(OEt)_2[CH_2 \cdot CH(OEt)_2]_2$. This is due to the rupture of the pyrone ring, a rupture which occurs much more readily in the pyrone than in the furan series. The acetal is colourless, distils at 279–282° (corr.), has a sp. gr. 0·982 at 0°/4°, and is only sparingly soluble in cold water. When shaken with twenty times its weight of 1 per cent. hydrochloric acid, it is hydrolysed to *bishydroxymethyleneacetone*, which has been isolated as the *copper* derivative, $C_5H_4O_3Cu$. Pyrone is obtained when the monomethyl ether is distilled, or the monobenzoate is heated at its melting point or boiled with light petroleum (b. p. 100–140°). The benzoate of the methyl ether and the mono- and di-benzoates of the hydroxy-compound are quantitatively converted into pyrone by ethereal hydrogen chloride.

3-*Methylpyrone* distils at 108–113° under 11 mm. pressure, crystallises from light petroleum in prisms, melts at 66·5–67·2°, dissolves readily in water, ethyl alcohol, ethyl acetate, or benzene, and yields precipitates with ethereal solutions of hydrogen chloride, oxalic or prussic acids, but no precipitate with an alcoholic solution of calcium chloride.

Some of these reactions are used as arguments against Collie's formulæ for pyrone derivatives. J. J. S.

Action of Bromine on Ethyl Dimethylpyronedicarboxylate.

F. CARLO PALAZZO (*Chem. Centr.*, 1905, i, 1258–1259; from *Giorn. Sci. Nat. Econ.*, 25, 207–216. Compare Abstr., 1904, i, 762).—By the action of bromine on ethyl dimethylpyronedicarboxylate, a dibromo-derivative, $O \begin{array}{c} \diagup C(CH_2Br) : C(CO_2Et) \\ \diagdown C(CH_2Br) : C(CO_2Et) \end{array} CO$, and a tetrabromo-derivative, $O \begin{array}{c} \diagup C(CHBr_2) : C(CO_2Et) \\ \diagdown C(CHBr_2) : C(CO_2Et) \end{array} CO$, are formed together with a liquid. The

constitution of the bromo-derivatives has been proved by their synthetical formation by the action of carbon oxychloride on the copper salt of ethyl γ -monobromoacetoacetate (compare Epprecht, Abstr., 1894, i, 171). Conrad and Guthzeit's ester behaves with bromine, therefore, in a similar manner to other derivatives of 1:4-pyrone, which also form substitution products, although the molecule contains double linkings. The constitution of the ester may therefore be represented by the formula
$$\text{O} \begin{array}{c} \text{CMe:C(CO}_2\text{Et)} \\ \text{CMe:C(CO}_2\text{Et)} \end{array} \text{CO}.$$

The formation of malonic acid by the action of barium hydroxide on the ester (Abstr., 1891, 672) is explained by assuming that ethyl acetonedicarboxylate, $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, is formed as an intermediate product. Since the compound $\text{C}_7\text{H}_9\text{O}_4\text{N}$ is also obtained by the action of hydroxylamine in solutions which are not alkaline, the action is really one of hydrolysis.

The bromine derivatives of ethyl dimethylpyronedicarboxylate are prepared by adding a solution of bromine in carbon disulphide to a solution of the ester in the same solvent. The dibromo-derivative crystallises from alcohol in colourless plates, melts at 126° , and is soluble in dilute acetic acid, acetone, alcohol, ethyl acetate, benzene or chloroform, sparingly so in ether or light petroleum, but almost insoluble in water.

The tetrabromo-derivative, obtained by evaporating the carbon disulphide mother liquor, crystallises from dilute acetic acid or carbon disulphide in octahedra, melts at 142° , and is readily soluble in acetone, benzene, or chloroform, less so in alcohol or acetic acid, and insoluble in water or light petroleum. A fluorescent solution is formed by adding a few drops of ammonia to a solution of the tetrabromo-derivative in acetone. An intensely yellow solution is formed by adding an alkali to an alcoholic solution, and potassium permanganate is instantly reduced. Both bromo-derivatives yield hydrogen bromide, carbon dioxide, acetone, and alcohol when boiled with an aqueous solution of an alkali, and both on reduction with zinc and acetic acid form ethyl dimethylpyronedicarboxylate; the latter was identified by converting it into ethyl lutidonedicarboxylate (Abstr., 1887, i, 502).

E. W. W.

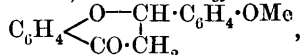
3:5-Diacetyl-2:6-dimethylpyrone and the Constitution of the Synthetical γ -Pyrone Compounds. F. CARLO PALAZZO and P. ONORATO (*Chem. Centr.*, 1905, i, 1259—1260; from *Giorn. Sci. Nat. Econ.*, 25, 217—238. Compare preceding abstract).—Whilst accepting Collie's formula for diacetyl dimethyl- γ -pyrone (*Trans.*, 1904, 971; compare also Thomas and Lefèvre, Abstr., 1889, i, 235), the authors point out the impossibility of dividing the pyrones into two classes according to their basic properties. The varying basicity of the pyrones is more probably due to the influence of the substituting groups in accordance with Willstätter and Pummerer's theory of the constitution of pyrones (Abstr., 1904, i, 1043).

3:5-Diacetyl-2:6-dimethylpyrone,
$$\text{O} \begin{array}{c} \text{CMe:CAc} \\ \text{CMe:CAc} \end{array} \text{CO},$$
 crystallises from alcohol in long, lustrous needles, melts at $124\text{--}125^\circ$, and is

soluble in light petroleum, ether, carbon disulphide, acetic acid, benzene, toluene, chloroform, or acetone, but only sparingly so in water; it sublimes in a vacuum without decomposing. When boiled with a 5 per cent. solution of barium hydroxide, it is decomposed, forming carbon dioxide, acetone, and acetic acid, and by the action of an alcoholic solution of ammonia it yields 3:5-diacetyl-2:6-dimethylpyridone, $\text{NH} \begin{array}{c} \text{CMe:Cac} \\ \text{CMe:Cac} \end{array} \text{CO}$, which crystallises from ethyl acetate in white, lustrous needles and melts at 232° . The *anhydride of a dioxime*, $\text{O} \begin{array}{c} \text{CMe:C} \cdot \text{CMe:N} \\ \text{CMe:C} \cdot \text{CMe:N} \end{array} \text{CO} \text{O}$, formed by the action of hydroxylamine on diacetyldimethylpyrone, crystallises from light petroleum and melts at 68° . The yellow substance, formed by the action of light on the compound $\text{C}_{11}\text{H}_{12}\text{O}_4$, appears to be merely another form of the same compound. Solutions of the yellow compound in benzene, toluene, chloroform, carbon disulphide, or ether are yellow. The colourless alcoholic solution requires a comparatively long exposure to sunlight before it becomes yellow. The yellow solutions gradually become colourless in diffused light. E. W. W.

Action of Carbonyl Chloride on the Copper Derivative of Benzoylacetone and on Dithiobenzoylacetone. VICTOR VAILLANT (*Bull. Soc. chim.*, 1905, [iii], 33, 458—460. Compare Abstr., 1896, i, 591, and Feist, Abstr., 1891, 459).—When dithiobenzoylacetone, dissolved in benzene, or the copper derivative of benzoylacetone, suspended in benzene, is treated with carbonyl chloride dissolved in toluene, 3:5-diacetyl-2:6-diphenylpyrone, $\text{O} \begin{array}{c} \text{PhC:Cac} \\ \text{PhC:Cac} \end{array} \text{CO}$, is formed, which crystallises from boiling alcohol in colourless needles, sinters at 175° , melts at $178\text{--}180^\circ$, is readily soluble in chloroform or benzene, and gives a red coloration with solution of ferric chloride after some hours, indicating that it is hydrolysed by this reagent into a β -diketonic substance. T. A. H.

4'-Hydroxyflavonol. ANNA EDELSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, 38, 1507—1509. Compare Gutzeit and Kostanecki, this vol., i, 366).—4'-Methoxyflavanone,



prepared by boiling an alcoholic solution of 2'-hydroxy-4-methoxychalkone with dilute sulphuric acid, crystallises from alcohol in plates and melts at 97° .

3-isoNitroso-4'-methoxyflavanone, $\text{C}_{16}\text{H}_{13}\text{O}_4\text{N}$, prepared from methoxyflavonone, amyl nitrite, and hydrochloric acid, separates from dilute alcohol as a yellow, crystalline powder and, when boiled with dilute mineral acids, forms 4'-methoxyflavonol, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ | \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{array}$, which separates from alcohol in pale yellow, glistening needles and melts at 225° . The latter compound produces a bright yellow shade

with aluminium mordants ; it forms a yellow *sodium* salt and dissolves in concentrated sulphuric acid to a fluorescent solution ; its *acetyl* derivative separates from dilute alcohol in colourless needles and melts at 138—139°. When 4'-methoxyflavonol is boiled with hydriodic acid, it forms 4'-*hydroxyflavonol*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$, which separates from alcohol in yellow needles and melts at 276°. Its solutions in dilute aqueous sodium hydroxide and in concentrated sulphuric acid respectively are fluorescent, whilst it yields a yellow shade with aluminium mordants ; its *diacetyl* derivative melts at 158°.

A. McK.

Phenothioxins. FERDINAND MAUTHNER (*Ber.*, 1905, **38**, 1411—1415).

—1 : 3-*Dinitrophenothioxin*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_2$, prepared by the reduction of *o*-dihydroxydiphenyl disulphide with sodium amalgam to thiocatechol and subsequent condensation of this with picryl chloride in alcoholic solution, crystallises in orange-red plates melting at 187° ; it dissolves in concentrated sulphuric acid to a red solution. 1 : 3-*Diaminophenothioxin*, prepared by reducing the dinitro-compound with tin and hydrochloric acid, crystallises in colourless needles melting at 158° ; the *sulphate* forms colourless needles. 1 : 3-*Diacetyldiaminophenothioxin* separates from alcohol in colourless needles melting at 224—225° ; 1 : 3-*dibenzoyl diaminophenoxthin* melts at 257°.

1 : 3-*Dinitrophenothioxin oxide*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \text{SO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_2$, prepared by oxidation with dilute nitric acid, crystallises in yellow needles, melts at 202—203°, and dissolves in concentrated sulphuric acid to a blood-red solution.

1 : 3-*Dinitrophenothioxin dioxide*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \text{SO}_2 \end{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_2$, formed on oxidising dinitrophenoxthin with chromic acid, crystallises from benzene in pale yellow needles melting at 256·5—257°. Stannous chloride reduces it to 1 : 3-*diaminodiphenothioxin dioxide*, which crystallises in colourless needles and melts at 228°.

E. F. A.

Formation of Inactive Arginine. E. PROVAN CATHCART (*Proc. Physiol. Soc.*, 1905, xxxix—xl ; *J. Physiol.*, **32**).—The conditions usually associated with racemisation phenomena, namely, high temperature and powerful reagents, are more nearly realised in the case of acid than in enzyme hydrolysis, yet it is the latter which (in some cases) yields the racemic arginine. This is more remarkable in view of the belief that an enzyme molecule is asymmetric. Some suggestions are offered as explanations, and experiments are being continued.

W. D. H.

Salts of the Hexone Bases with Picrolonic Acid. HERMANN STEUDEL (*Zeit. physiol. Chem.*, 1905, **44**, 157—158).—Arginine picrolonate has the composition $\text{C}_{16}\text{H}_{22}\text{O}_7\text{N}_8$, that is, it is formed by the union of 1 mol. of base with one of acid, and not with two, as pre-

viously stated (Abstr., 1903, i, 431). Histidine picrolonate has the composition $C_{10}H_8O_5N_4 \cdot C_6H_5O_2N_3$. Details of the preparation of picrolonic acid are given.

J. J. S.

Corydalis Alkaloids. JOHANNES GADAMER (*Arch. Pharm.*, 1905, 243, 147—154).—In part an introduction to the following abstracts; in part physiological (see this vol., ii, 411).

C. F. B.

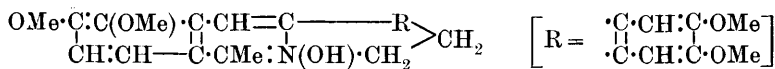
Alkaloids of the Subaerial Parts of *Corydalis cava* and *Corydalis solida*. OTTO HAARS (*Arch. Pharm.*, 1905, 243, 154—165).—From the leaves and stems of both of these plants, gathered at the flowering season, bulbocapnine was isolated; with the first of them the yield was 0.6 per cent. of the dried drug. From 18 kilos. of dried *Corydalis cava* there were also obtained 1.5 grams of a new alkaloid, $C_{21}H_{21}O_8N$; this melts at 230° ; unlike the other corydalis alkaloids it is levorotatory, having $[\alpha]_D - 112.8^\circ$ at 20° ; it was found to be a monacid base, the *platinichloride*, which melts at 214° , being analysed; it is insoluble in alkali hydroxides, and it contains no methoxyl groups.

Out of the alcoholic mother liquor, from which the alkaloids just mentioned had been obtained, 0.5 gram of another new alkaloid, $C_{21}H_{23}O_7N$ or $C_{21}H_{25}O_7N$, was isolated; this melts at 137.5° , has $[\alpha]_D + 96.8^\circ$ at 20° , and exhibits triboluminescence; it contains two OMe and one NMe groups.

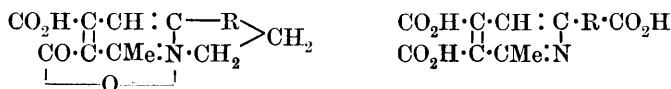
Protopine could not be detected.

C. F. B.

Constitution of Corydaline. OTTO HAARS (*Arch. Pharm.*, 1905, 243, 165—197. Compare Dobbie and Lauder, *Trans.*, 1897, 71, 657; 1902, 81, 145, &c.).—The author has repeated much of the work of Dobbie and Lauder, and obtained substantially the same results. A few discrepancies and additional observations are detailed below; some of these lead to the following formulæ, which differ slightly from those of Dobbie and Lauder:



Dehydrocorydaline.



Corydyl Acid.

Corydyllic Acid.

Dehydrocorydaline in solution is a quaternary ammonium base. In the free state it melts and decomposes at 112 — 113° , has the composition $C_{22}H_{25}O_5N$, and must be regarded as a ψ -base with the keto-composition, containing the groups $\cdot \text{CMeO}$ and $\text{NH} <$ instead of $\cdot \text{CMe} \cdot \text{N}(\text{OH}) <$, for it forms an *oxime* (compare Gadamer, this vol., i, 368), $C_{22}H_{26}O_5N_2$, which melts and decomposes at 165° , and it condenses with *p*-aminodimethylaniline yielding the product, $C_{30}H_{35}O_4N_3$, which melts at 120 — 130° .

An attempt to resolve the optically inactive corydaline melting at 135° (Gadamer, Abstr., 1902, i, 307) into its active constituents was unsuccessful. Yet probably this substance should be regarded as *r*-corydaline, each active constituent of which has either both asymmetric carbon atoms *d*, or both *l*. The inactive corydaline melting at 158° has been separated partially into its active constituents, and neither of these is identical with the active corydaline that occurs naturally; probably this inactive variety should be regarded as *r*-mesocorydaline, in the two active constituents of which the two asymmetric carbon atoms are respectively *d:l* and *l:d*.

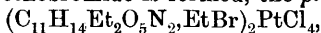
Corydic acid, $C_{18}H_{15}O_6N$, was obtained crystallised with $1H_2O$ in transparent rhombohedra, melting at 224° , and with $2H_2O$ in yellow needles, melting at 218° . It is to be regarded as a betaine-acid, for it reacts like a monobasic acid with aqueous potassium hydroxide, and, when heated with methyl-alcoholic potassium hydroxide and methyl iodide, it forms the *iodide* of the *dimethyl ester*, $C_{20}H_{22}O_6NI \cdot 4H_2O$, which has the character of a quaternary ammonium iodide. This salt melts at 100° ; the corresponding *chloride*, with $4H_2O$, *platinichloride*, with $2H_2O$, and *aurichloride*, the last melting at 145° , were also analysed. *Ethyl corydate hydriodide* was also prepared; it melts at 112° .

Corydilic acid, $C_{17}H_{15}O_5N$, was obtained crystallised with $2H_2O$. It has the character of a tertiary base; for, when it is heated with methyl-alcoholic potassium hydroxide and methyl iodide, it forms *trimethyl corydilate methiodide*, $C_{21}H_{24}O_5NI$, which melts at 142° ; the corresponding *nitrate* melts at 102° .

Corydaldine crystallises in the monoclinic system [$a:b:c = 1.6181:1:2.7827$; $\beta = 125^{\circ}52'$]. C. F. B.

Pilocarpine. VI. ADOLF PINNER (*Ber.*, 1905, 38, 1510—1531. Compare Abstr., 1901, i, 340; 1902, i, 232, 638).—Now that it has been established that pilocarpine is a glyoxaline derivative with the probable constitution $\begin{array}{c} \text{CHEt} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NMe} \\ \text{CO} \cdot \text{O} \cdot \text{CH}_2 \quad \quad \quad \text{CH} \cdot \text{N} \end{array} \gg \text{CH}$, the author has studied the constitution of certain derivatives of pilocarpine and of isopilocarpine.

When the requisite amount of sulphuric acid is added to barium pilocarpoate, and the aqueous solution, after removal of the barium sulphate, is concentrated, a syrup is obtained, on the addition of alcohol to which the substance $C_{11}H_{14}O_4N_2$ is formed; it crystallises in glistening prisms, melts at 180° , and has acid properties. When heated at 200 — 210° , it forms *isopilocarpoic acid*, $C_{11}H_{16}O_5N_2$, which crystallises in needles and melts at 150° . *Ethyl isopilocarpoate*, $C_{11}H_{14}Et_2O_5N_2$, prepared by the esterification of pilocarpoic acid or of isopilocarpoic acid with ethyl alcohol, is an oil; its *hydrochloride* forms deliquescent crystals; its *platinichloride* melts at 200° . When pilocarpoic acid is heated for 10 hours at 100° with potassium hydroxide and an excess of ethyl bromide, a mixture of ethyl isopilocarpoate and its ethobromide is formed, the *platinichloride*,



of the latter compound melting at 107° and decomposing at about 190° .

By the oxidation of pilocarpoic acid with potassium permanganate, α -ethyltricarballic acid, $C_8H_{12}O_6$, melting at $145-146^\circ$, is formed, and not pilomalic acid, $C_7H_{12}O_5$, as previously described by the author. The α -ethyltricarballic acid thus prepared is optically active, whilst Jowett's acid, prepared by fusion of homopilopie acid with potassium hydroxide, is optically inactive and melts at 157° (Trans., 1901, **79**, 1331). The author confirms Jowett's observations on the behaviour of the calcium salt (Trans., 1901, **79**, 1344). When the crude ester, prepared from the acid, alcoholic potassium hydroxide, and ethyl bromide, is heated at 100° for 72 hours with methyl alcohol and ammonia, α -ethyltricarballic triamide, $C_8H_9O_3(NH_2)_3$, crystallising in needles, is formed; it begins to decompose at 265° .

By the action of ethyl alcohol on the crude acid chloride, obtained by the action of phosphorus oxychloride on α -ethyltricarballic acid, a mixture of the tri-, di-, and mono-ethyl esters is formed, the latter preponderating.

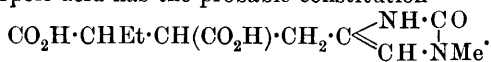
Bromocarpic acid, $C_{10}H_{15}O_4N_2Br$, dissolves in a warm concentrated aqueous solution of barium hydroxide, and is reprecipitated when this solution is acidified. When heated with barium hydroxide solution for 8 to 10 hours at 130° , ammonia, methylamine, barium carbonate, and barium pilomalate are produced, but not barium oxalate; the action is represented as follows: $C_{10}H_{15}O_4N_2Br_2 + 2O + 3H_2O = HBr + 3CO_2 + NH_3 + CH_3 \cdot NH_2 + C_7H_{12}O_5$.

When dibromoisopilocarpinic acid, $C_{11}H_{14}O_4N_2Br_2$, is added to a concentrated warm aqueous solution of barium hydroxide, the solution soon becomes turbid, owing to the separation of barium oxalate; when the alkaline filtrate is distilled, ammonia and methylamine are formed, whilst barium carbonate separates. If, however, the excess of barium hydroxide is removed by carbon dioxide before the ammonia and methylamine are distilled off, and the solution then evaporated to a small bulk and alcohol added, barium pilomalate separates, whilst the solution contains methylcarbamide.

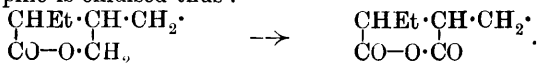
When dibromoisopilocarpinic acid is heated with an excess of aqueous calcium hydroxide, solutions are obtained from which, on the addition of alcohol, calcium salts containing nitrogen are precipitated. The analyses of these salts point to the existence of an acid, $C_{11}H_{15}O_7N$.

When isopilocarpine or its hydrochloride is heated with bromine and water, bromoisopilocarpine perbromide, $C_{11}H_{15}O_2N_2Br \cdot HBr_3$, is produced; it forms reddish-yellow prisms and melts at 123° . Bromoisopilocarpine is formed by the action of sulphurous acid on it. This product is probably identical with Jowett's bromoisopilocarpine.

*iso*Pilocarpoic acid has the probable constitution

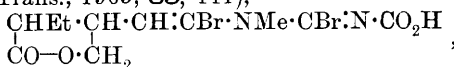


During the formation of pilocarpoic acid by the oxidation of pilocarpine with chromic acid, the lactone portion of the group $C_7H_{11}O_2$ in pilocarpine is oxidised thus:

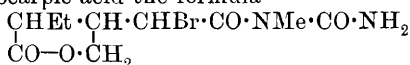


By the action of barium hydroxide, the latter group then yields the group $\text{CO}_2\text{H}\cdot\text{CH}(\text{Et})\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot$.

The author considers that Jowett's formula for dibromoisopilocarpinic acid (Trans., 1903, 83, 441),



is incorrect. He suggests the formula $\begin{array}{c} \text{CH}(\text{Et})\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CBr}\cdot\text{NH} \\ \text{CO}-\text{O}\cdot\text{CH}_2 \quad \text{CO}\cdot\text{NMe} \end{array} > \text{CO}$, whilst for bromocarpic acid the formula



is suggested.

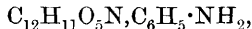
A. McK.

Thiopyrrolidone. JULIUS TAFEL and PAUL LAVACZEK (*Ber.*, 1905, 38, 1592).—If a mixture of pyrrolidone and phosphorus trisulphide is heated at 150° , and, after evolution of hydrogen sulphide, cooled, powdered, and heated in a retort, at 350° , *thiopyrrolidone*, $\text{C}_4\text{H}_7\text{NS}$, distils as a yellow oil. On recrystallisation from a mixture of benzene and light petroleum, it forms colourless needles melting at 114° .

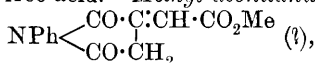
G. Y.

Action of Aniline on Anhydrocarboxylic Acids. W. BERTRAM (*Ber.*, 1905, 38, 1615—1625).—In studying the action of aniline on anhydroaconitic acid, anhydroacetylcitronic acid, and other similar acids, the author has encountered a class of compounds which are both anilides and carboxylic acids. He proposes the name *anilidic acids* for these compounds, since the term anilic acids is used for the additive products of aniline and the anhydrides of dicarboxylic acids.

Aconite-monoanilidic acid, $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, obtained by the interaction of molecular proportions of aniline and anhydroaconitic acid in ethereal solution, crystallises from alcohol in yellow needles melting and decomposing at 141° , and dissolves readily in methyl alcohol or acetone. The *aniline salt*,



prepared by the action of aniline (2 mols.) on anhydroaconitic acid (1 mol.), crystallises from methyl alcohol in silky leaflets which decompose and give up aniline even in the absence of light and air; it melts at 107 — 108° and dissolves readily in alcohols and its acetone solution deposits the free acid. *Methyl aconitanilate*,



crystallises in white leaflets or needles melting at 143° ; it dissolves slightly in water, giving a neutral solution, and more readily in alcohols; on reduction with aluminium and acetic acid, this ester and also the ethyl and propyl esters yield the corresponding esters of tricarballylanilic acid, identical with those obtained by passing hydrogen chloride into the alcoholic solutions of aniline tricarballylanilate (*vide infra*). The *ethyl ester*, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$, crystallises in needles melting at 112° . The *propyl ester*, $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}$, is readily soluble in benzene and crystallises in needles

melting at 106°. The anilide, $C_{18}H_{14}O_3N_2$, prepared by the action of 3 mols. of aniline on 1 mol. of anhydroaconitic acid, has already been obtained by Pebal (*Annalen*, 1856, **98**, 79) and by Skinner and Ruhemann (*Trans.*, 1889, **55**, 238).

Aconitic trimethylamide, $C_3H_3(CO \cdot NHMe)_3$, prepared by passing dry methylamine into an ice-cold solution of ethyl aconitate in an equal volume of ether, separates from ether in colourless, acicular crystals melting at 213—215°.

Aniline tricarballylmonoanilidate,

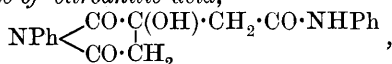
$CO_2H \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO \cdot NHPh, C_6H_5 \cdot NH_2$ (?), prepared by the interaction of aniline (2 mols.) and anhydrotricarballylic acid, crystallises from alcohol in white needles melting at 127—128°, and is slightly soluble in benzene or water.

Methyl tricarballylanilate, $NPh \begin{matrix} \diagup CO \cdot CH \cdot CH_2 \cdot CO_2Me \\ \diagdown CO \cdot CH_2 \end{matrix}$, prepared by passing hydrogen chloride into an ice-cold saturated methyl-alcoholic solution of aniline tricarballylmonoanilidate, forms prismatic crystals melting at 106°, and is readily soluble in alcohols. The corresponding *ethyl* ester, $C_{14}H_{15}O_4N$, crystallises in slender, silky needles melting at 90°. The *propyl* ester, $C_{15}H_{17}O_4N$, crystallises in needles melting at about 55°. The *anilide of tricarballylanilic acid*, $C_{18}H_{16}O_3N_2$, crystallises in needles melting at 168° and has a neutral reaction.

The action of excess of aniline (more than 4 mols.) on anhydroacetylcitric acid (1 mol.) in ethereal solution yields: (1) *citrodianilidic acid*, $OH \cdot C(CH_2 \cdot CO \cdot NHPh)_2 \cdot CO_2H$, crystallises in slender leaflets melting and decomposing at 181°; on heating with 20 per cent. hydrochloric acid, it yields citric acid. When heated under about 12 mm. pressure, it gives carbon dioxide, water, aniline, citraconanil, a *substance* separating from alcohol in almost colourless plates, melting at 115°, and a *compound*, $C_{11}H_9O_2N$, which crystallises in metallic-looking, yellowish-green leaflets melting at 235—237°, and is moderately soluble in acetic acid or phenol.

(2) *Aniline citrodianilidate*, $C_{18}H_{18}O_5N_2, C_6H_5 \cdot NH_2$, which separates in white needles melting at 152°.

(3) The *anilide of citroanilic acid*,



which crystallises in compact octahedra or long, silky needles melting at 182°.

Potassium citrodianilidate, $C_{18}H_{17}O_5N_2K$, crystallises in needles.

T. H. P.

Influence of Indifferent Solvents on the Alkylation of Organic Bases. ADOLF PINNER and A. FRANZ (*Ber.*, 1905, **38**, 1539—1548).—During the alkylation of organic bases, in addition to the rate of the reaction and the strength of the base, the solubility of the additive product in the solvent used is an important factor.

The base used was dissolved in an equal weight of solvent and the alkyl haloid added, the solution being kept cold. In certain cases, where the reaction was vigorous, an excess of solvent was taken. After

24—48 hours, the liquid was filtered and the amount of halogen in the crystalline residue was estimated. In such cases where the crystalline residue was suspected to contain quaternary salt, the residue was made alkaline with sodium hydroxide, extracted with ether, and the amount of halogen, both in the ether solution and in the liquid extracted, estimated.

By the action of methyl iodide (1 mol.) on piperidine (1 mol.) in ethereal solution, the salt of the secondary base, together with the quaternary ammonium salt, is formed; when methyl iodide (1 mol.) acts on piperidine (2 mols.), a mixture of the salt of the secondary base and the free tertiary base is formed.

When ethyl bromide (1 mol.) acts on piperidine (2 mols.), piperidine hydrobromide (1 mol.) and ethylpiperidine (1 mol.) are formed. The influence of the solvent was examined.

The behaviour of alkyl bromide was similar to that of ethyl bromide.

Amylpiperidine is best prepared, when ether is used as the solvent, from amyl bromide (1 mol.) and piperidine (2 mols.).

When ethyl chloroacetate acts on piperidine in ethereal solution at the ordinary temperature, the piperidine salt and ethyl piperidylacetate, $C_5NH_{10} \cdot CH_2 \cdot CO_2Et$, are formed.

When benzyl chloride (1 mol.) acts on piperidine (1 mol.) in ethereal solution, piperidine hydrochloride is formed, whilst benzylpiperidine is present in the ethereal solution. When alcohol is used instead of ether as the solvent, a mixture of piperidine and benzylpiperidine salts is formed.

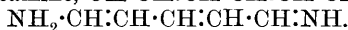
When ethyl bromide (1 mol.) acts on dipropylamine (1 mol.) at the ordinary temperature, dipropylamine hydrobromide is formed, whilst at 100° a mixture of the dipropylamine salt and the ethyldipropylamine salt is formed. This mixture is also produced when alcohol is used as a solvent and when the interaction takes place at the ordinary temperature; at 100° , the ethyldipropylamine salt only is formed.

By the interaction of molecular amounts of ethylamine and ethyl bromide, a mixture containing the salts of the primary and secondary bases, and possibly also of the tertiary base, is formed; in ethereal solution, the free tertiary base remains dissolved. The action of ethyl bromide on amylamine is similar.

When molecular quantities of benzylamine and ethyl bromide interact in ethereal solution, benzylamine salt separates, whilst benzylethylamine remains in the ethereal solution.

A. MCK.

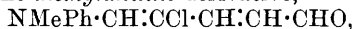
Dinitrophenylpyridinium Chloride and its Transformation Products. III. THEODOR ZINCKE (*Annalen*, 1905, 339, 193—201).—It has been shown previously (Abstr., 1904, i, 448) that the dyes obtained from dinitrophenylpyridinium chloride and primary and secondary bases are the derivatives of an aldehyde alcohol or the corresponding imineamine, $OH \cdot CH : CH \cdot CH : CH \cdot CHO$ or



By the decomposition of phenol in alkaline solution by chlorine, Hantzsch (Abstr., 1889, 853) obtained an acid, $C_6H_5O_4Cl_3$, which was finally converted into a compound, $C_5H_5O_2Cl$, thought to be a

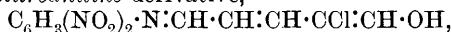
cyclic diketone. Ince (Abstr., 1890, 1090) obtained coloured anilides and toluidides from this compound. It is now shown that this compound is the chloroaldehyde alcohol, $\text{OH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$, and that it yields coloured anilides analogous to those previously described.

It is unnecessary to isolate the compound $\text{C}_6\text{H}_5\text{O}_2\text{Cl}$, but the sodium salt, $\text{C}_6\text{H}_4\text{O}_4\text{ClNa}$, is directly treated with a solution of aniline in hydrochloric acid, when the dye begins to separate as *hydrochloride*, $\text{NHClPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NHPh}$; it forms dark red leaflets, melting at $128-129^\circ$, and is converted into phenylchloropyridinium chloride by boiling with hydrochloric acid; the *chloride*, $\text{C}_5\text{NH}_4\text{PhCl}_2$, crystallises in needles; the *platinichloride*, $(\text{C}_{17}\text{H}_{16}\text{N}_2\text{Cl})_2\cdot\text{PtCl}_6$, crystallises in orange-red prisms or needles melting and decomposing at $195-196^\circ$. The *oxime*, $\text{NHPh}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NOH}$, prepared from the dianilide, crystallises in yellow needles melting and decomposing at 152° . The *methylaniline* derivative,



crystallises in yellow needles melting at $126-127^\circ$; it does not react with methylaniline, but with primary amines or phenylhydrazine; the *anilide*, $\text{NHPhCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NMePh}$, crystallises in red needles melting and decomposing at $125-126^\circ$, the *p-chloroaniline* derivative, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NHCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NMePh}$, crystallises in red needles melting and decomposing at $130-132^\circ$. The *phenylhydrazone*, $\text{NHPh}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{NMePh}$, forms yellow needles or leaflets melting and decomposing at 147° .

The 2:4-dinitroaniline derivative,

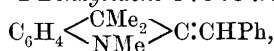


prepared from the sodium salt, forms dark red crystals melting and decomposing at 180° , and yields a phenylpyridinium chloride with hydrochloric acid.

K. J. P. O.

Transformation of Indolinones into Alkylene Indolines.

KARL BRUNNER (*Ber.*, 1905, **38**, 1359—1362. Compare Abstr., 1896, i, 625; 1897, i, 100, 438; 1898, i, 360, 384, 682; Decker and Hock, Abstr., 1904, i, 620).—2-Benzylidene-1:3:3-trimethylindoline,



prepared by decomposing with dilute acid the product of the action of magnesium benzyl chloride on 1:3:3-trimethylindoline-2-one in ethereal solution, crystallises from methyl alcohol in long, colourless needles, melts at 93° , and boils at 212° under 24 mm. pressure; the *hydriodide*, $\text{C}_{18}\text{H}_{20}\text{NI}$, crystallises from alcohol in yellow nodules melting and decomposing at 180° , the *platinichloride* forms orange-red leaflets and melts at 188° and the *stannichloride* melts at 186° . The base is rapidly oxidised by alkaline potassium permanganate; a warm alkaline solution of potassium ferricyanide converts it into 1:3:3-trimethylindoline-2-one, benzoic acid, and traces of benzaldehyde. W. A. D.

Preparation of Indophenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 157288).—The direct oxidation of a mixture of phenols and *p*-aminophenols to indophenols has not hitherto been

practicable. The oxidation takes place satisfactorily, however, at low temperatures. The solution of alkali phenoxide and *p*-aminophenol is added to a solution containing sodium hypochlorite, sodium chloride, and ice at a temperature of -16° to -17° . The oxidation takes place rapidly, and the sodium derivative of the indophenol is precipitated in green, glistening crystals. The products dissolve in dilute alkali hydroxides to blue solutions, from which acids precipitate brownish-red powders, soluble in alcohol, ether, or chloroform.

C. H. D.

Ammonium Compounds. XIX. Nitration of Quaternary cycloAmmonium Nitrates. HERMAN DECKER [with ST. GADOMSKA and M. GIRARD] (*Ber.*, 1905, 38, 1274—1280. Compare this vol., i, 374).—*Quinoline methonitrate*, $C_9NH_7Me \cdot NO_3$, formed by adding the powdered methiodide to nitric acid of sp. gr. 1.4, is obtained on evaporation of the acid as a hygroscopic, white, crystalline mass, which melts at about 84° . When treated with nitric and sulphuric acids at the laboratory temperature, the methonitrate yields a mixture of 5- and 8-nitroquinoline methonitrates, which melts at about 190° . The isomerides cannot be separated as methonitrates, but after conversion into the methiodides and heating at 150° , 8-nitroquinoline is extracted by light petroleum, leaving 5-nitroquinoline methiodide.

8-Nitroquinoline methonitrate, $C_{10}H_9O_5N_3$, formed from 8-nitroquinoline methiodide or methosulphate, crystallises in yellow, hygroscopic needles and melts and decomposes at 160 — 170° .

5-Nitroquinoline methonitrate closely resembles the 8-nitro-compound, and melts and decomposes at 202 — 205° .

6-Bromoquinoline methonitrate forms white crystals, darkens at 220° , melts and decomposes at 228° , and on nitration and conversion into the methiodide yields 6-bromo-5-nitroquinoline methiodide.

3-Bromoquinoline methonitrate crystallises in white needles, becomes yellow at 160° , melts and decomposes at 207° , and on nitration yields 3-bromo-5-nitroquinoline methonitrate, which crystallises in yellow scales, melts and decomposes at 159° , and is not hygroscopic.

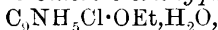
8-Methylquinoline methonitrate, $C_{11}H_{12}O_3N_2$, forms white crystals, melts at about 72° , is very easily soluble in water, and on nitration and oxidation of the product with alkaline potassium ferricyanide yields 5-nitro-1 : 8-dimethylquinoline.

6-Methylquinoline methonitrate crystallises in white, hygroscopic needles, and on nitration and treatment with methyl iodide yields 5-nitro-6-methylquinoline methiodide.

When nitrated at 35 — 40° , the additive compound of papaverine and methyl sulphate yields nitropapaverine methonitrate, which, when boiled in dilute alkaline solution, forms nitrobromoveratrole and dimethoxymethylisoquinolone.

G. Y.

Replacement of Bromine by Chlorine in Quinoline Derivatives and Halogenated 8-Hydroxyquinolones. JOH. HOWITZ and KURT WITTE (*Ber.*, 1905, 38, 1260—1270. Compare *Abstr.*, 1903, i, 279; this vol., i, 375).—5-Chloro-6-ethoxyquinoline,



formed by boiling 5-chloro-6-hydroxyquinoline with sodium hydroxide and ethyl bromide in alcoholic solution in a reflux apparatus, crystallises in yellow needles, which weather on exposure to the air, and melts at 75°. The *methiodide*, $C_{12}H_{13}ONCl \cdot H_2O$, forms red prisms and melts and decomposes at 187°; the *ethiodide* forms slender, yellow needles or thick, red crystals and melts at 206°. 5-Chloro-6-ethoxy-1-methylquinolone, $C_9NH_4OClMe \cdot OEt$, is formed by the oxidation of the methiodide with potassium ferricyanide in cooled alkaline solution; it crystallises in yellow needles, melts at 136°, and, when heated with concentrated hydrochloric acid at 160–170°, yields 5-chloro-6-hydroxy-1-methylquinolone (Abstr., 1903, i, 279). 5-Chloro-6-ethoxy-1-ethylquinolone, formed by oxidation of the ethiodide with potassium ferricyanide, crystallises in clear plates containing $3H_2O$, melts at 72°, or, when anhydrous, at 102°, and when heated with concentrated hydrochloric acid at 160–170° yields 5-chloro-6-hydroxy-1-ethylquinolone (*loc. cit.*).

7-Bromo-8-methoxyquinoline, formed by boiling 7-bromo-8-hydroxyquinoline with sodium hydroxide and methyl iodide in methyl-alcoholic solution, crystallises in slender needles and melts at 78°. The *methiodide* crystallises in brown needles and melts and decomposes at 154°. 7-Bromo-8-methoxy-1-methylquinolone, formed by oxidation of the methiodide with alkaline potassium ferricyanide, crystallises in small prisms and melts at 75°, and when boiled with hydrobromic acid yields 7-bromo-8-hydroxy-1-methylquinolone, which crystallises in small, colourless needles, melts at 176°, and forms a sparingly soluble *sodium* derivative. Hydrolysis of the bromomethoxymethylquinolone with concentrated hydrochloric acid at 160° leads to the formation of 7-chloro-8-hydroxy-1-methylquinolone, $C_{10}H_8O_2NCl \cdot H_2O$, which crystallises in colourless needles, loses H_2O at 110°, and melts at 247°.

5-Bromo-8-methoxyquinoline, $C_{10}H_8ONBr \cdot 3H_2O$, formed by boiling the hydroxyquinoline with sodium hydroxide, methyl iodide, and methyl alcohol, crystallises in slender, colourless needles, which weather on exposure to the air; it melts at 82°. The *methiodide* forms flat, brown crystals and melts at 161°. 5-Bromo-8-methoxy-1-methylquinolone, obtained by oxidation of the methiodide, crystallises in slender, felted needles, melts at 145°, and when boiled with concentrated hydrobromic acid, yields 5-bromo-8-hydroxy-1-methylquinolone, which crystallises in small, colourless needles, melts at 207°, and forms a sparingly soluble *sodium* salt. Hydrolysis of the bromomethoxy-compound with concentrated hydrochloric acid at 170° leads to the formation of 5-chloro-8-hydroxy-1-methylquinolone, which crystallises in colourless needles and melts at 251°.

5:7-Dibromo-8-methoxyquinoline, $C_{10}H_7ONBr_2$, crystallises in slender needles, which slowly become violet, and melts at 99°. The *methiodide* crystallises in brown needles, melts at 174°, and on oxidation is converted into 5:7-dibromo-8-methoxy-1-methylquinolone, which forms slender, yellow needles and melts at 166°. 5:7-Dibromo-8-hydroxy-1-methylquinolone crystallises from glacial acetic acid in transparent, yellow needles, which contain acetic acid, and on exposure to the air rapidly weather to a powder, melting at 209°. 5:7-Dichloro-8-

hydroxy-1-methylquinolone, obtained by heating dibromomethoxy-methylquinolone with concentrated hydrochloric acid at 160—170°, crystallises in glistening needles and melts at 258°.

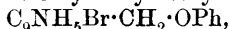
5-Bromo-6-hydroxy-, 5-bromo-8-hydroxy-, 7-bromo-8-hydroxy-, and 5:7-dibromo-8-hydroxy-quinolines yield the corresponding bromo-hydroxyquinolines when heated with concentrated hydrochloric acid at 160—170°. G. Y.

Derivatives of 8-Quinolinealdehyde. JOH. HOWITZ and WILHELM SCHWENK (*Ber.*, 1905, **38**, 1280—1289. Compare Abstr., 1902, i, 397).—The *hydrochloride* of 8-quinolinealdehyde,



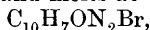
forms white crystals and melts at 213°; the *hydriodide* forms nodular aggregates of red crystals and melts and decomposes at 228°. The *oxime*, $\text{C}_9\text{NH}_6\cdot\text{CH}:\text{NOH}, \frac{1}{2}\text{H}_2\text{O}$, crystallises in small, glistening leaflets and melts at 115°. The *anil*, $\text{C}_9\text{NH}_6\cdot\text{CH}:\text{NPh}$, forms yellow crystals and melts at 82°; the *o-tolil*, $\text{C}_{10}\text{H}_7\text{N}:\text{N}\cdot\text{C}_7\text{H}_7$, crystallises in yellow needles and melts at 105°. The *azine*, $\text{C}_9\text{NH}_6\cdot\text{CH}:\text{N}:\text{N}:\text{CH}\cdot\text{C}_9\text{NH}_6$, crystallises in slender, yellow needles and melts at 248—249°; the *phenylhydrazone*, $\text{C}_9\text{NH}_6\cdot\text{CH}:\text{N}:\text{NHPH}$, crystallises in yellow needles and melts at 176°; the *semicarbazone*, $\text{C}_{11}\text{H}_{10}\text{ON}_4$, crystallises in slender, white needles and melts at 238—239°. When heated with dimethylaniline and zinc chloride, 8-quinolinealdehyde forms tetramethyldi-aminodiphenyl-8-quinoly methane, $\text{C}_9\text{NH}_6\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, which crystallises in colourless needles, melts at 179—180°, and when oxidised by lead peroxide yields an intense green *dye*; this forms a green, crystalline *zincchloride*.

3-Bromo-8-bromomethylquinoline, $\text{C}_9\text{NH}_5\text{Br}\cdot\text{CH}_2\text{Br}$, is formed in small amount in the preparation of 8-bromomethylquinoline, or in large amount by heating the dibromide of 8-methylquinoline hydrobromide at 180° until the evolution of hydrogen bromide ceases, and then adding 1 mol. of bromine. It crystallises in glistening, silvery leaflets, melts at 106°, and is a weak base; the *platinichloride* forms a yellow, crystalline precipitate. When boiled with alcoholic potassium hydroxide in a reflux apparatus, the dibromo-compound forms 3-bromo-8-hydroxymethylquinoline, $\text{C}_9\text{NH}_5\text{Br}\cdot\text{CH}_2\cdot\text{OH}$, which crystallises in white needles, melts at 51°, and is oxidised by potassium permanganate in alkaline solution to 5-bromopyridine-2:3-dicarboxylic acid. The *phenyl ether* of 3-bromo-8-hydroxymethylquinoline,



is formed by boiling 3-bromo-8-bromomethylquinoline with potassium phenoxide in alcoholic solution; it crystallises in long, white needles and melts at 102—103°.

3-Bromo-8-quinolinealdehyde, $\text{C}_9\text{NH}_5\text{Br}\cdot\text{CHO}$, formed by the oxidation of the corresponding alcohol with nitric acid of sp. gr. 1.4, crystallises in white needles and melts at 168°. The *oxime*,



crystallises in slender, white needles and melts at 188°; the *azine*, $\text{C}_{20}\text{H}_{12}\text{N}_4\text{Br}_2$, crystallises in yellow needles and melts at 268°; the *anil*, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{Br}$, forms long, yellow needles and melts at 142°; the

semicarbazone, $C_{11}H_9ON_4Br$, crystallises in white needles and melts at 250° .

3-Bromoquinoline-8-carboxylic acid, $C_9NH_5Br \cdot CO_2H$, formed by oxidation of the aldehyde with chromic acid in sulphuric acid solution, crystallises in glistening, slender, white needles, melts at $206-207^\circ$, and sublimes without decomposition. The barium salt,

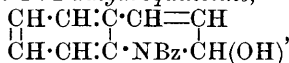


crystallises in glistening, slender, white needles.

8-Bromomethylquinoline cannot be oxidised directly to 8-quinoline-aldehyde, but is converted by alcoholic potassium hydroxide into 8-hydroxymethylquinoline, which is oxidised to the aldehyde by nitric acid. G. Y.

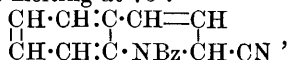
Introduction of the Benzoyl Group into Tertiary Cyclic Bases. ARNOLD REISSERT (*Ber.*, 1905, 38, 1603—1614).—Although pyridine reacts very energetically with acid chlorides, forming additive compounds, quinoline exhibits no analogous reaction. In presence of sodium hydroxide or potassium cyanide, however, quinoline and benzoyl chloride react, giving the following products.

2-Hydroxy-1-benzoyl-1 : 2-dihydroquinoline,



prepared by the action of excess of benzoyl chloride on quinoline in presence of sodium hydroxide, crystallises from alcohol in shining, colourless needles melting at 182° , and dissolves readily in acetic acid. By acetic acid or dilute mineral acids, it is converted into benzoic acid and quinoline, whilst concentrated sulphuric acid transforms it into reddish-yellow, resinous products. It is dissolved and gradually decomposed by alcoholic sodium hydroxide solution. On oxidation with potassium permanganate in the cold, it yields benzoylanthranilic acid, isatinic acid, and a small proportion of a compound which crystallises from aqueous alcohol in slender needles melting at 73° .

2-Cyano-1-benzoyl-1 : 2-dihydroquinoline,



obtained by the action of benzoyl chloride on quinoline in presence of potassium cyanide, crystallises from alcohol in hard, shining prisms melting at $154-155^\circ$, and is readily soluble in benzene, chloroform, acetone, or acetic acid. By means of concentrated mineral acids, it is resolved into benzaldehyde, quinaldinic acid and its amide, and the benzoic ester of quinoline-2-carboxylic acid, $C_9H_6N \cdot CO \cdot O \cdot CHPhBz$, which crystallises from alcohol in microscopic, pointed prisms melting at $168-168.5^\circ$ and is readily soluble in benzene, acetic acid, ethyl acetate, chloroform, or acetone, and slightly so in methyl or ethyl alcohol. T. H. P.

Papaverinium Bases. III. HERMAN DECKER and OTTO KOCH (*Ber.*, 1905, 38, 1739—1741. Compare *Abstr.*, 1904, i, 338, 926).—Dimethoxyisoquinoline methiodide, $C_{12}H_{14}O_2NI \cdot H_2O$, prepared by the action of methyl iodide or of methyl sulphate on dimethoxyisoquinoline, melts at $236-237^\circ$. The picrate melts at 209° and is explosive.

Dimethoxy-2-methylisoquinolone, prepared by the action of an excess of potassium ferricyanide on the methiodide, separates as a flocculent mass, which yields the hydrochloride melting at 185—186°.

Dimethoxy-2-benzylisoquinolone, prepared from benzyl chloride and dimethoxyisoquinoline in an analogous manner, melts at 165° and is identical with the product previously prepared from benzylisopapaverine (*loc. cit.*).

Piperonyl alcohol is best prepared by Cannizaro's method. When a current of benzene is passed into a solution of piperonyl alcohol in benzene at 0°, *piperonyl chloride* is formed; it crystallises in white needles, melts at 23°, and does not form a magnesium compound when its ethereal or anisole solution is heated with magnesium. A. McK.

Stereoisomeric Conhydrinium Iodides. MAX SCHOLTZ and P. PAWLICKI (*Ber.*, 1905, **38**, 1289—1295. Compare Abstr., 1904, i, 1044; this vol., i, 296).—Conhydrine has $[\alpha]_D + 10^\circ$. 1-Ethylconhydrine boils at 227—228° (corr.) and has a sp. gr. 0.9345 at 20°/4°, $[\alpha]_D - 45.2^\circ$, and $[M]_D - 77^\circ$.

By the action of benzyl iodide on 1-ethylconhydrine, a mixture of two stereoisomeric benzylethylconhydrinium iodides is formed; these can be separated by fractional precipitation by ether from the chloroform solution. The α -iodide, $C_{17}H_{28}ONI$, which is the more soluble in the mixture of chloroform and ether, melts at 163°; the β -iodide melts at 188°. These two iodides yield the same derivatives; the *platinichloride* crystallises from water and melts at 191°; the *mercurichloride* and *picrate* are oils. By the action of ethyl iodide on 1-ethylconhydrine, only Wertheim's diethylconhydrinium iodide (*Jahresber.*, 1863, 435) is formed.

1-Propylconhydrine boils at 240—241° (corr.) and has a sp. gr. 0.9172 at 20°/4°, $[\alpha]_D - 50.1^\circ$, and $[M]_D - 93^\circ$. With benzyl iodide, it forms a mixture of two stereoisomeric benzylpropylconhydrinium iodides, which are separated by recrystallisation from water. The α -iodide, $C_{18}H_{30}ONI \cdot 2H_2O$, crystallises in glistening, short prisms on slow evaporation of its aqueous solution, melts at 55°, loses $2H_2O$ at 100°, and, when anhydrous, melts and changes into the β -isomeride at 161°. The β -iodide crystallises from water in colourless needles and melts at 180°. Both iodides give the same crystalline *platinichloride*, which melts at 201—202°.

1-isoAmylconhydrine is a colourless oil, which boils at 272—273° (corr.) and has a sp. gr. 0.9087, $[\alpha]_D - 45.1^\circ$, and $[M]_D - 96^\circ$. A mixture of two stereoisomeric benzylisoamylconhydrinium iodides, which can be separated by recrystallisation from water, is formed by the action of benzyl iodide on *N*-isoamylconhydrine. The α -iodide, $C_{20}H_{34}ONI$, which is the more soluble in water, melts at 165° and has $[\alpha]_D - 40^\circ$ at 20°; the β -iodide melts at 185° and has $[\alpha]_D - 50^\circ$ at 20°. Both iodides yield the same *platinichloride*, $(C_{20}H_{34}ON)_2PtCl_6$, which melts at 195°, and *mercurichloride*, which melts at 197°.

1-Ethyl-2-methyltetrahydroquinoline, formed by the action of ethyl iodide and potassium hydroxide on dextrorotatory 2-methyltetrahydroquinoline (Ladenberg, Abstr., 1894, i, 208), boils at 256° (corr.), has

a sp. gr. 0.9942 at $20^{\circ}/4^{\circ}$ and $[\alpha]_D +12.1^{\circ}$ at 20° , and, when warmed with benzyl iodide, forms only one 1-benzyl-1-ethyl-2-methyltetrahydroquinolinium iodide, $C_{19}H_{24}NI$, which crystallises in orange-red leaflets and melts at 161° . G. Y.

Benzidine Salts (Hydrofluoride and Hydrosilicofluoride). RICHARD EHRENFELD (*Chem. Zeit.*, 1905, 29, 422—424).—When benzidine is heated with an excess of hydrofluoric acid, a mixture of the salts $C_{12}H_8(NH_2)_2 \cdot 5HF$ and $C_{12}H_8(NH_2)_2 \cdot 6HF$ is formed. At the ordinary temperature, benzidine interacts with hydrofluoric acid to form the salt $C_{12}H_8(NH_2)_2 \cdot 2HF$, and sometimes, under certain conditions, it yields the salt $C_{12}H_8(NH_2)_2 \cdot 3HF$.

Solutions of benzidine hydrochloride were added to solutions of ammonium fluoride and sodium fluoride respectively, which were heated to boiling in platinum vessels. The number of molecules of hydrogen fluoride with which benzidine combines under these conditions depends on the amount of free hydrochloric acid in the solution of benzidine hydrochloride added. Benzidine may unite with from 1 to 6 mols. of hydrogen fluoride.

The salt $C_{12}H_8(NH_2)_2 \cdot H_2SiF_6$, prepared by the action of boiling hydrofluosilicic acid on a solution of benzidine hydrochloride, forms silvery, hexagonal crystals. A. McK.

Constitution of Diketobutyric Ester Phenylhydrazones. ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], 33, 490—495. Compare Abstr., 1904, i, 556, 789, and this vol., i, 408).—Most of the results recorded in this paper have already been published (Abstr., 1904, i, 789). The product of the action of *p*-nitrophenylhydrazine on ethyl diketobutyrate β -phenylhydrazone is now regarded as 1-phenyl-3-methyl-5-pyrazolone-4-*p*-nitrophenylhydrazone (compare Bülow, Abstr., 1899, i, 271). By the action of phenylhydrazine on ethyl diketobutyrate, dissolved in boiling alcohol or in ether, in presence of zinc chloride, 1-phenyl-3-methyl-5-pyrazolone-4-phenylhydrazone is formed (compare Abstr., 1904, i, 789). The author considers that this synthesis affords a new proof of the hydrazinic constitution of this compound advocated by Sachs and Barschall (Abstr., 1902, i, 503) as against the azoic constitution proposed by Bülow (Abstr., 1899, i, 356, and Eibner, 1903, i, 871). T. A. H.

Hydrazones derived from *o*-, *m*-, and *p*-Nitrophenylhydrazines. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Rec. trav. chim.*, 1905, 24, 33—39. Compare Abstr., 1904, i, 98).—Methods are described for the estimation of acetone, diethyl ketone, acetaldehyde, and benzaldehyde, and for the separation of dextrose, lævulose, or mannose from sucrose, by the conversion of these aldehydes or ketones into their respective *p*-nitrophenylhydrazones. It is probable that the same method may also be applied to the separation of the hexoses from maltose and lactose, since the *p*-nitrophenylhydrazones of the latter are readily soluble.

Glycuronic acid p-nitrophenylhydrazone forms yellow crystals, melts at 225° , has $[\alpha]_D -91.2^{\circ}$ (in pyridine and ethyl alcohol), and dissolves in warm water, sparingly in alcohol, ether, and chloroform. This

derivative may be used for the detection of small quantities of the acid. *Lyxose p-nitrophenylhydrazone* separates from alcohol in yellow crystals, melts at 172° , and has $[\alpha]_D + 32.2^{\circ}$.

The *m-nitrophenylhydrazones* of the following aldehydes and ketones were prepared by warming them, dissolved in alcohol, for a few minutes with *m*-nitrophenylhydrazine : diethyl ketone (m. p. 105°), *o*-, *m*-, and *p*-nitrobenzaldehydes (m. p. 205° , 213° , and 228° respectively), benzophenone (m. p. 138°), acetophenone (m. p. 163°), salicylaldehyde (m. p. 197°), *p*-tolualdehyde, (m. p. 155°), cinnamaldehyde (m. p. 146°), and furfuraldehyde (m. p. 137°).

Dextrose m-nitrophenylhydrazone melts at 110° and has $\alpha_D - 6.3^{\circ}$; the corresponding derivative of mannose melts at 162° and has $\alpha_D + 10.7^{\circ}$, that of galactose melts at 182° and is optically inactive, that of rhamnose melts at 156° and has $\alpha_D - 21.4^{\circ}$, and the *arabinose* compound melts at 182° and is optically inactive. These derivatives of the hexoses crystallise readily, are yellow, soluble in boiling alcohol, sparingly soluble in water, and the respective sugars are regenerated on treatment with benzaldehyde.

The *o-nitrophenylhydrazones* of the following substances were prepared : acetone (m. p. 70°), diethyl ketone (m. p. 60°), formaldehyde (m. p. 85°), acetaldehyde (m. p. 124°), *o*-, *m*-, and *p*-nitrobenzaldehydes (m. p. 225° , 230° , and 255° respectively), *o*- and *p*-hydroxybenzaldehydes (m. p. 193° and 235° respectively), *p*-tolualdehyde (m. p. 183°), acetophenone (m. p. 138°), benzophenone (m. p. 161°), furfuraldehyde (m. p. 155°), and cinnamaldehyde (m. p. 190°).

The *o-nitrophenylhydrazone* of dextrose melts at 158° and has $\alpha_D + 27.8^{\circ}$, and the corresponding derivatives of lævulose (m. p. 162° , $\alpha_D + 31^{\circ}$), mannose (m. p. 171° , $\alpha_D + 16^{\circ}$), galactose (m. p. 178° , $\alpha_D - 26.8^{\circ}$), rhamnose (m. p. 162° , $\alpha_D - 59^{\circ}$), and arabinose (m. p. 172° , $\alpha_D - 21.4^{\circ}$) were prepared. Lævulose-*o*-nitrophenylhydrazone, which crystallises in bright red needles, is less soluble in alcohol than the dextrose derivative, and it is possible to separate these two sugars by this means. Galactose-*o*-nitrophenylhydrazone is gelatinous and in this respect resembles the benzylallyl- and phenyl-allyl-hydrazones of this sugar. T. A. H.

Antipyrilsemicarbazide. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and H. BARBIER (*Bull. Soc. chim.*, 1905, [iii], 33, 503—505).—*Antipyrilsemicarbazide*, $\begin{array}{c} \text{NMe} \cdot \text{CMe} \\ | \\ \text{NPh} - \text{CO} \end{array} \text{C} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$, prepared by the

action of hydrazine on antipyrilcarbamide, is a crystalline powder, melts at 135° , and is readily soluble in water or alcohol, less so in ether or benzene. The salts are difficult to crystallise. The *acetyl* derivative crystallises from boiling alcohol in colourless needles and melts at 214 — 215° . *β -Propylideneantipyrilsemicarbazide*, obtained by condensing acetone with antipyrilsemicarbazide, forms colourless crystals and melts at 209 — 210° . *Benzylideneantipyrilsemicarbazide* occurs in colourless needles and melts at 225° , and the corresponding product prepared from ethyl acetoacetate crystallises from alcohol in needles and melts at 207° . With phenylcarbimide, antipyrilsemicarbazide yields the corresponding *phenylcarbamide*, which is crystalline and melts

at 236°, and with ethyl chlorocarbonate the corresponding *urethane*, which occurs in colourless needles and melts at 207°. T. A. H.

Glyoxalines. ADOLF PINNER (*Ber.*, 1905, **38**, 1531—1538).—By the action of ammonia on phenylglyoxal, a mixture of the isomerides 2-benzoyl-5-phenylglyoxaline and 3-hydroxy-1:4-diphenylpyrazine melting at 202° is produced (compare Abstr., 1903, i, 123). By the action of methyl iodide on the former compound, a methiodide is formed from which, by the action of potassium hydroxide, methylamine is eliminated, whilst the latter compound forms a methyl ether.

2-Benzoyl-5-phenylglyoxaline, $\begin{array}{c} \text{NH-CBz} \\ | \\ \text{CPh:CH} \end{array} \gg \text{N}$, separates from pyridine in yellow prisms and melts at 280°. It reacts with methyl iodide and potassium hydroxide at 100° to form 2-benzoyl-5-phenyl-1-methylglyoxaline methiodide, which melts and decomposes at 216°.

Phenylglyoxaline, $\begin{array}{c} \text{NH-CH} \\ | \\ \text{CPh:CH} \end{array} \gg \text{N}$, when heated for 8 hours at 100° with a mixture of ethyl bromide and alcohol, forms 5-phenyl-1-ethylglyoxaline, $\begin{array}{c} \text{NEt-CH} \\ | \\ \text{CPh:CH} \end{array} \gg \text{N}$, the *platinichloride* of which melts and decomposes at 197°. When boiled with an aqueous solution of sodium hydroxide, phenylethylglyoxaline yields ethylamine.

Diphenylglyoxaline is best prepared by the action of ammonia on a mixture of formaldehyde and benzil at a low temperature. 4:5-Diphenyl-1-ethylglyoxaline, $\begin{array}{c} \text{NEt-CH} \\ | \\ \text{CPh:CPh} \end{array} \gg \text{N}$, prepared by the alkylation of diphenylglyoxaline by ethyl bromide, forms rhombic prisms and melts at 94—95°; its *hydrochloride* forms rhombic prisms and decomposes at 260°; its *platinichloride* melts and decomposes at 225°, whilst its *hydrobromide* forms glistening, rhombic crystals, which melt and decompose at 260°.

4:5-Diphenyl-1:3-diethylglyoxalinium bromide, $\begin{array}{c} \text{NEt-CH} \\ | \\ \text{CPh:CPh} \end{array} \gg \text{NEtBr}$, crystallises in glistening prisms and melts at 153—154°. When boiled with an aqueous solution of potassium hydroxide, ethylamine and a carblyamine are formed. A. McK.

5-Aminopyrazole and Iminopyrine. AUGUST MICHAELIS (*Annalen*, 1905, **339**, 117—193).—The pyrimines are derivatives of the pyrazoles, in which an alkyl group is attached to the nitrogen atom in position 2, and have a bivalent group or atom, oxygen, sulphur, selenium, or the imino-group, attached at the same time to position 2 and either position 3 or 5; the nitrogen atom in position 2 is there-

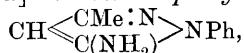
fore quinquivalent, thus: $\begin{array}{c} \text{—C:NAlk.} \\ | \\ \text{NPh} \\ | \\ \text{—C:C—} \end{array} \gg \text{NH (or O, S, or Se) or}$
 $\begin{array}{c} \text{—C} \begin{array}{c} \text{NPh} \cdot \text{NAlk.} \\ \diagup \quad \diagdown \end{array} \text{—C—} \end{array} \gg \text{NH (or O, S, or Se).}$

Knorr, on the other hand, thinks that there is only one ring, the bivalent atom or group being linked exclusively to position 3 or 5.

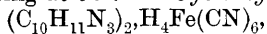
The name "iminopyrine" is given to the 1-phenyl-2:3-dimethyl-iminopyrazole, which corresponds with antipyrine. The iminopyrines are prepared either by the action of alkali hydroxides on the methiodide of 5-aminopyrazoles or from antipyrine chlorides (5-chloropyrazole-methiodide) by the action of ammonia or a primary amine. They are strong bases, either liquid or solid, which absorb carbon dioxide from the air. They form additive compounds with alkyl iodides, the

second ring being broken, thus: $\begin{array}{c} -\text{C}=\text{N}(\text{AlkI}) \\ -\text{C}:\text{C}(\text{NMePh}) \end{array} > \text{NPh}$. Similarly, acid chlorides combine with the iminopyrines, forming compounds which are strong bases. The conductivity and other properties of the solutions point to their containing an ammonium hydroxide formed from the iminopyrine by addition of water, the second ring being broken, thus: $\begin{array}{c} -\text{C}:\text{NMe}(\text{OH}) \\ -\text{C}:\text{C}(\text{NHX}) \end{array} > \text{NPh}$. On addition of alkali, the anhydride, that is, the iminopyrine, is again formed.

[With EDUARD BRUST.]—5-Amino-1-phenyl-3-methylpyrazole,



prepared by heating under pressure a mixture of antipyrine chloride and ammonium carbonate at 300°, crystallises in needles melting at 116° and boiling at 333°; it reduces silver, but not Fehling's solution; it gives an intense red precipitate with potassium bismuth iodide, and a blue coloration with a mixture of ferric chloride and potassium ferricyanide. Bleaching powder in the presence of acetic acid converts it into a red compound containing chlorine, whilst nitrous acid leads to the formation of a compound $\text{C}_{10}\text{H}_8\text{ON}_4$; the hydrochloride, $\text{C}_{10}\text{H}_{11}\text{N}_3\cdot\text{HCl}$, is a powder melting at 198°. The mercurichloride, $\text{C}_{10}\text{H}_{11}\text{N}_3\cdot\text{HgCl}_2$, is a white precipitate decomposed on heating. The platinichloride, $(\text{C}_{10}\text{H}_{11}\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in reddish-yellow needles melting at 169°; the aurichloride is a reddish-brown precipitate melting at 90°. The ferrocyanide,



crystallises in leaflets, and the picrate, $\text{C}_{10}\text{H}_{11}\text{N}_3\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, in yellow scales melting at 160—162°. 5-Acetyl-amino-1-phenyl-3-methylpyrazole is a crystalline solid melting at 110°, and does not give a coloration

with bleaching powder; its chloro-derivative, $\text{CCl} \begin{array}{c} \text{CMe}=\text{N} \\ \text{C}(\text{NHAc}) \end{array} > \text{NPh}$,

prepared by leading chlorine into its acetic acid solution, crystallises in needles melting at 132—133°. On hydrolysis, it yields 4-chloro-5-amino-1-phenyl-3-methylpyrazole, which can also be obtained directly from the 5-amino-compound; it crystallises in yellow needles melting at 118°. Prolonged chlorination of the aminopyrazole results in the formation of the hydrochloride of 4-chloro-5-amino-1-dichlorophenyl-3-

methylpyrazole, $\text{CCl} \begin{array}{c} \text{CMe}:\text{N} \\ \text{C}(\text{NH}_2) \end{array} > \text{N}\cdot\text{C}_6\text{H}_3\text{Cl}_2$, which is decomposed by

water, the base being a yellow solid decomposing on heating. 4-Bromo-5-amino-1-phenyl-3-methylpyrazole, $\text{C}_{10}\text{H}_{10}\text{N}_3\text{Br}$, prepared by brominating aminopyrazole, crystallises in scales melting at 106.5°; the corresponding iodo-compound crystallises in leaflets melting at 75°, and gives a white precipitate with mercuric chloride. 4-Benzeneazo-5-

amino-1-phenyl-3-methylpyrazole, prepared from the aminopyrazole and diazobenzene, crystallises in dark yellow leaflets melting at 140° ; its *hydrochloride* is dark red and melts at 170° . 5-*Amino-1-nitro-phenyl-3-methylpyrazole*, $\text{CH} \begin{smallmatrix} \text{CMe:N} \\ \text{C(NH}_2\text{)} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, prepared by nitrating the aminopyrazole, is a yellow solid melting at $98-99^{\circ}$.

5-*Ethylamino-1-phenyl-3-methylpyrazole*, prepared by heating antipyrine chloride and anhydrous ethylamine at 150° , is a liquid boiling at 315° and gives, with mercuric chloride, a white double salt. The corresponding *dimethylamine* derivative is a yellow oil boiling at 297° , and the *diethylamine* derivative a yellow oil boiling at $306-307^{\circ}$; the *platinichloride* of the latter, $(\text{C}_{14}\text{H}_{19}\text{N}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, crystallises in reddish-yellow leaflets melting at 168° .

5-*Amino-1-phenyl-3:4-dimethylpyrazole*, prepared by heating the methiodide of chlorophenyldimethylpyrazole with ammonium carbonate at 250° , forms white crystals melting at 102° and boiling at 336° ; the *hydrochloride* forms white crystals melting at 70° , and the *picrate* yellow crystals melting at $137-138^{\circ}$. It also yields a *nitro-derivative* melting at 87° .

The *methiodide* of 5-*amino-1-phenyl-3-methylpyrazole* (*iminopyr-ine hydriodide*), $\begin{smallmatrix} \text{CMe:N(MeI)} \\ \text{CH:C(NH}_2\text{)} \end{smallmatrix} \text{NPh}$, prepared by heating 5-*amino- pyrazole* with methyl iodide at 100° , forms crystals melting at 182° ; it also crystallises with $\frac{1}{2}\text{H}_2\text{O}$, and then sinters at 83° and melts at 163° . The *platinichloride*, $(\text{C}_{11}\text{H}_{14}\text{N}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, melts at 207° . The free *iminopyrine* can be prepared from the iodide or, better, from the chloride by treatment with sodium hydroxide. The corresponding *ethyliminopyrine hydriodide* crystallises in needles melting at $206-207^{\circ}$. 2:5-*Imino-1-phenyl-3-methyl-2-ethylpyrazole* (2-*ethylimino-*

pyrine), $\text{C} \begin{smallmatrix} \text{CH:CMe} \\ \text{NPh} \\ \text{NH} \end{smallmatrix} \text{NEt}$, prepared from the compound last men-

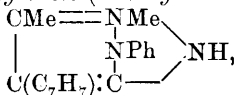
tioned or by treatment of the ethiodide of 5-*iodo-1-phenyl-3-methyl- pyrazole* with ammonia at 180° , is a thick yellow oil. The *platinichloride* crystallises in red needles melting at $192-195^{\circ}$; the *picrate* forms yellow prisms melting at 172° , and the *benzenesulphonic* deriv-ative colourless crystals melting at 173° .

[With WILHELM PREUNER.]—5-*Amino-1-phenyl-4-benzyl-3-methyl- pyrazole*, $\text{C}_7\text{H}_7 \cdot \text{C} \begin{smallmatrix} \text{CMe:N} \\ \text{C(NH}_2\text{)} \end{smallmatrix} \text{NPh}$, prepared by heating the methiodide of 5-chloro-4-benzylpyrazole with ammonium carbonate under pressure at 210° , forms colourless crystals melting at 77° ; the *hydrochloride* crystallises in microscopic needles melting at 187° , and the *picrate* in yellow needles melting at 140° ; the *benzoyl* derivative crystallises in prisms melting at 184° .

1-*Phenyl-4-benzyl-3-methylpyrazolone* appears to exist in two modifica-tions; if in the preparation of 5-chloro-1-phenyl-4-benzyl-3-methyl- pyrazole from it a small quantity of phosphorus oxychloride is used, colourless crystals of a modification of the pyrazolone are obtained melting at 147.5° , which pass slowly into the ordinary form melting at 136° .

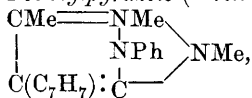
5-*Methylamino-1-phenyl-4-benzyl-3-methylpyrazole* (ψ -4-*benzylamino-*

pyrine), $C_7H_7 \cdot C \begin{smallmatrix} \text{CMe} = \text{N} \\ \text{C}(\text{NHMe}) \end{smallmatrix} > \text{NPh}$, is formed on distilling 4-benzyl-*iminopyrine* under reduced pressure, and crystallises in prisms melting at 120.5° and boiling at 236° under 17 mm. pressure. 2 : 5-*Imino-1-phenyl-4-benzyl-3-methylpyrazole* (4-benzyliminopyrine),



prepared from 4-benzylantipyrynechloride and ammonia, forms yellowish-white crystals melting at 96° , absorbs carbon dioxide from the air, and forms a *hydrochloride* which forms large crystals melting at 217° . The *mercurichloride*, $C_{18}H_{19}N_3 \cdot HgCl_2$, crystallises in yellow prisms melting at 129° ; the *platinichloride*, $(C_{18}H_{19}N_3)_2 \cdot H_2PtCl_6$, is a reddish-yellow precipitate melting at 96° , and passing, on heating, into the salt of 5-aminopyrazole. The *picrate*, $C_{18}H_{19}N_3 \cdot C_6H_3O_7N_3$, forms golden-yellow leaflets melting at 147° ; the *carbonate* is a white powder melting at 131° and having a strongly alkaline reaction.

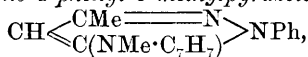
The methochloride of 5-chloro-1-phenyl-4-benzylpyrazole (antipyryne chloride) was prepared from the methiodide and silver chloride, and is a hygroscopic powder melting at 148° . When heated with benzoyl chloride in benzene solution, *benzoyl-4-benzyliminopyrine* is obtained as crystals melting at 124° and has an alkaline reaction. The *benzenesulphonic* compound forms crystals melting at 141° . 2 : 5-*Methylimino-1-phenyl-2 : 3-dimethyl-4-benzylpyrazole* (4-benzylmethyliminopyrine),



is prepared as hydriodide from methyl iodide and 5-methylamino-1-phenyl-3-methyl-4-benzylpyrazole; the *carbonate* forms white crusts with H_2O , melting at 121° .

[With RICHARD BLUME.]—5-*Benzylamino-1-phenyl-3-methylpyrazole*, $CH \begin{smallmatrix} \text{CMe} = \text{N} \\ \text{C}(\text{NAc} \cdot \text{C}_7\text{H}_7) \end{smallmatrix} > \text{NPh}$, prepared from antipyryne chloride and benzylamine, is a viscous, yellow oil boiling at 228° under 12 mm. pressure; its *hydrochloride* is microcrystalline powder melting at 159° , and its *platinichloride*, $(C_{17}H_{17}N_3)_2 \cdot H_2PtCl_6 \cdot H_2O$, forms brownish-red crystals melting at 109° . The *mercurichloride* forms white crystals melting at 129 — 130° . The acyl derivatives can only be obtained indirectly by heating 2 : 5-benzyliminopyrine with acetyl or benzoyl chloride; the *acetyl* derivative crystallises in leaflets melting at 114° and boiling at 240 — 245° under 18 mm. pressure; it is basic and forms a *hydrochloride* crystallising in leaflets melting at 203° . The *benzoyl* derivative forms white crystals melting at 121° and boiling at 253° under 18 mm. pressure.

5-*Benzylmethylamino-1-phenyl-3-methylpyrazole*,



prepared from antipyryne chloride and benzylmethylamine, is a viscous yellow oil boiling at 242° under 20 mm. pressure; its *platinichloride* forms reddish-brown crystals melting at 74° . 5-*Dibenzylamino-1-phenyl-3-methylpyrazole*, prepared by distilling under reduced pressure the benzylchloride of benzyliminopyrine, forms colourless crystals

melting at 106° and boiling at 272° under 18 mm. pressure; the *hydrochloride* forms crystals melting at 148° , and the *platinichloride*, $(C_{24}H_{23}N_3)_2 \cdot H_2PtCl_6$, brownish-red prisms melting at 178° .

2:5-Benzylimino-1-phenyl-2:3-dimethylpyrazole (2:5-benzyliminopyr-
ine), $\begin{array}{c} \text{CMe:NMe} \\ | \\ \text{NPh} \\ | \\ \text{CH=C} \end{array} \rangle \text{N} \cdot \text{C}_7\text{H}_7$, prepared from antipyrine chloride and

benzylamine, is a viscous, yellow oil, strongly basic, absorbing carbon dioxide from the air; its *hydrochloride* is hygroscopic, and its *platinichloride*, $(C_{18}H_{19}N_3)_2 \cdot H_2PtCl_6$, forms reddish-brown needles melting at 196° . The *aurichloride* crystallises in brown needles melting at 105° , and the *mercurichloride* white needles melting at 110° ; the *carbonate* is hygroscopic, and the *hydriodide*, which is identical with the methiodide from 5-benzylamino-1-phenyl-3-methylpyrazole, crystallises in colourless prisms melting at 159° ; the *ferrocyanide* is a white precipitate, and the *picrate* crystallises in yellow leaflets melting at 138.5° .

The *methiodide* of benzyliminopyrine, $\text{CH} \begin{array}{c} \text{CMe=NMeI} \\ \text{C(NMe} \cdot \text{C}_7\text{H}_7) \end{array} \rangle \text{NPh}$, crystallises in prisms which become yellow in the air and melt at 115° ; on heating, methyl iodide is eliminated, and 5-methylbenzylamino-1-phenyl-3-methylpyrazole is formed. The *benzyl chloride* of benzyliminopyrine crystallises in prisms melting at 80° , and the *benzyl iodide* in prisms melting at 158° . The *acetyl iodide*, $\begin{array}{c} \text{CMe} \\ || \\ \text{CH:C(NAc} \cdot \text{C}_7\text{H}_7) \end{array} \rangle \text{NPh}$, prepared from the hygroscopic acetyl chloride by potassium iodide, crystallises in prisms melting at 156° ; the *benzoyl chloride* forms quadratic crystals melting at 100° , and yields a *platinichloride*, $(C_{25}H_{21}N_3OCl)_2 \cdot PtCl_4$, as a pale brown, crystalline powder melting at 206° . The *benzoyl iodide* forms white crystals melting at 51° .

[With ALBERT HEPNER.]—2:5-Phenylimino-1-phenyl-2:3-methyl-
pyrazole (anilopyrine), $\begin{array}{c} \text{CMe:NMe} \\ | \\ \text{NPh} \\ | \\ \text{CH=C} \end{array} \rangle \text{NPh}$, prepared by heating the

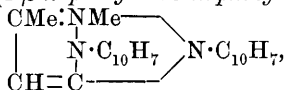
methiodide of 5-chloro-1-phenyl-3-methylpyrazole with aniline at 125° and decomposing the hydriodide with sodium hydroxide, forms crystals melting at $79-80^{\circ}$. Its *acetyl iodide*, prepared from the hygroscopic acetyl chloride, crystallises in needles melting at 204° , the *benzoyl chloride* forms white prisms melting at 214° , and when heated loses methyl iodide, yielding benzoylanilinophenylmethylpyrazole. The *benzoyl iodide* crystallises in prisms melting at 210° . 5-Benzoylanilino-1-phenyl-3-methylpyrazole, $\text{CH} \begin{array}{c} \text{CMe} \\ || \\ \text{C(NPhBz)} \end{array} \rangle \text{NPh}$, prepared as just mentioned, melts at 135° and boils at 200° under 16 mm. pressure.

2:5-Naphthylimino-1-phenyl-2:3-dimethylpyrazole (2:5-naphthyl-
iminopyrine), $\begin{array}{c} \text{CMe:NMe} \\ | \\ \text{N} \cdot \text{C}_{10}\text{H}_7 \\ | \\ \text{CH=C} \end{array} \rangle \text{NPh}$, prepared from antipyrine chloride

and β -naphthylamine, crystallises in greenish-yellow plates melting at 70° , and on heating yields 3-methylamino-1-phenyl-5- β -naphthylpyrazole, which crystallises in brown needles melting at 125° . The *platinichloride* of the naphthyliminopyryne, $(C_{21}H_{19}N_3)_2 \cdot H_2PtCl_6$, crystallises in yellow needles melting at 157 – 163° . The *hydriodide* crystallises in needles melting at 178° . 2:5- α -Naphthylimino-1-phenyl-2:3-dimethylpyrazole (2:5- α -naphthyliminopyryne) crystallises in yellowish-green plates or needles melting at 161 – 162° ; its *platinichloride* forms reddish-yellow crystals decomposing at 196 – 200° ; the *hydriodide* forms white crystals melting at 220° , and the *methiodide* needles with H_2O melting at 210° .

[With WILHELM DANZFUSS.]—The *methochloride* of chloro- β -naphthylmethylpyrazole (β -naphthylantipyryne chloride) is prepared from the methiodide and silver chloride, and crystallises in needles melting at 138° ; by treatment with aniline, it is converted into 2:5-phenylimino-1- β -naphthyl-2:3-dimethylpyrazole (1- β -naphthylanilopyryne), which crystallises in yellow leaflets melting at 182° ; the *platinichloride* forms reddish-brown leaflets melting at 214 – 215° , and the *hydriodide* white crystals melting at 179° , and the *methiodide* crystals melting at 163° . The *benzoyl chloride* forms hygroscopic crystals, and its *platinichloride*, with H_2O , a red precipitate melting at 242° . The *benzoyl iodide* crystallises in prisms melting and decomposing at 171° . The *acetyl iodide*, prepared from the acetyl chloride, crystallises in white prisms melting at 187° .

5-Anilino-1- β -naphthyl-3-methylpyrazole, prepared from 1- β -naphthylantipyryne chloride and aniline, crystallises in yellow needles melting at 122° . 5-Benzoylanilino-1- β -naphthyl-3-methylpyrazole is not formed on benzoylating the compound last mentioned, but by heating the benzoyl chloride of naphthylanilopyryne, and crystallises in needles melting at 128° and boiling at 265° under 13 mm. pressure. 5-Methylanilino-1- β -naphthyl-3-methylpyrazole, prepared from naphthylantipyryne chloride and methylaniline or by distilling the methiodide of naphthylanilopyryne, crystallises in leaflets melting at 113° and boiling at 245° under 13 mm. pressure; the *platinichloride* crystallises with $2H_2O$ in pale yellow needles melting at 132° . 2:5- β -Naphthylimino-1- β -naphthyl-2:3-dimethylpyrazole (1- β -naphthyl-2:5-naphthyliminopyryne),



prepared from naphthylantipyryne chloride and naphthylamine, crystallises in dark yellow needles, with $2H_2O$, melting at 68° , and when anhydrous at 122° ; the *platinichloride* crystallises with H_2O in leaflets melting and decomposing at 172° . The *hydriodide* of 5- α -naphthylimino-1- β -naphthyl-3-methylpyrazole, from which the free base cannot be isolated, yields, when heated, 5- α -naphthylamino-1- β -naphthyl-3-methylpyrazole, which forms crystals melting at 145° . K. J. P. O.

Bromodihydrouracil. SIEGMUND GABRIEL (*Ber.*, 1905, 38, 1689–1691. Compare this vol., i, 265).—When bromodihydrouracil (*Abstr.*, 1901, i, 294; this vol., i, 266) is boiled with an aqueous solution of sodium sulphite, it is transformed into dihydrouracil, and

when heated with alcoholic ammonia at 100° into uracil. *Thiocyanobromodihydrouracil*, $C_4H_4O_2N_2Br \cdot SCN$, obtained by brominating thiocyanodihydrouracil, crystallises from boiling water in large, four-sided prisms melting and decomposing at 182° .

2:6-Dichloropyrimidine, $CCl \langle \begin{smallmatrix} N-CH \\ N:CCl \end{smallmatrix} \rangle CH$, obtained by the action of phosphorus oxychloride on uracil at 140° , distils at $208.5-209.5^{\circ}$ under 773 mm. pressure, crystallises from light petroleum in compact needles, melts at 61° , and volatilises in the air. When heated with alcoholic ammonia at 100° for 2 hours, the chloro-base yields 2-amino-6-chloropyrimidine (Gabriel and Colman, *Abstr.*, 1904, i, 103) and 6-amino-2-chloropyrimidine. The latter crystallises from ethyl acetate in compact prisms, melts at $206-207^{\circ}$, and sublimes when carefully heated on a watch-glass. J. J. S.

Pyrimidines. VIII. Structure of Certain Derivatives. HENRY L. WHEELER and H. STANLEY BRISTOL (*Amer. Chem. J.*, 1905, 33, 437-448).—The following compounds have been prepared by the action of alkyl bromides on thiocarbamide. *ψ-Propylthiocarbamide hydrobromide* crystallises in long, colourless needles and melts at about 60° . *ψ-isoButylthiocarbamide hydrobromide* forms a fibrous mass of crystals and melts at about 96° . *ψ-isoAmylthiocarbamide hydrobromide* crystallises in long prisms and melts at about 84° .

The following substances have been obtained by the method described for the preparation of 6-oxy-2-methylthiopyrimidine (*Abstr.*, 1903, i, 524). 6-Oxy-2-propylthiopyrimidine, $NH \langle \begin{smallmatrix} C(SPr^a):N \\ CO-CH \end{smallmatrix} \rangle CH$, crystallises in long, colourless needles, melts at 117° , and is readily soluble in alcohol or hot water. 6-Oxy-2-isobutylthiopyrimidine forms leaf-like plates and melts at 107° . 6-Oxy-2-isoamylthiopyrimidine crystallises in long, thin plates and melts at 115° .

[With SAMUEL H. CLAPP.]—When uracil is heated at 125° with a mixture of concentrated sulphuric and fuming nitric acids, 5-nitrouracil is obtained.

By the reduction of 5-nitrouracil with aluminium amalgam, 5-amino-uracil is produced; its picrate melts and decomposes at $247-248^{\circ}$, and not at 147° , as stated by Behrend and Grünwald (*Abstr.*, 1900, i, 63).

By the action of a mixture of concentrated nitric and sulphuric acids on 6-oxy-2-ethylthiopyrimidine, 5-nitrouracil is produced. When 6-oxy-2-thiopyrimidine is treated with nitric acid, 5-nitrouracil is formed, together with another substance, which is probably 6-oxy-pyrimidine.

[By TREAT B. JOHNSON.]—Nitrouracil is also produced when 6-chloro-2-ethylthiopyrimidine is treated with a mixture of nitric and sulphuric acids.

When 5-bromouracil is warmed with a mixture of phosphorus pentachloride and phosphorus oxychloride, 2:6-dichloro-5-bromopyrimidine, $N \langle \begin{smallmatrix} CCl=N \\ CCl \cdot CBr \end{smallmatrix} \rangle CH$, is produced, which boils at $119-120^{\circ}$ under 17-18 mm. pressure, and on cooling solidifies to a crystalline

mass and melts at about -3° ; by the action of aniline on this compound, 5-bromo-2:6-dianilinopyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{NHPh})=\text{N} \\ \text{C}(\text{NHPh})\cdot\text{CBr} \end{smallmatrix} \text{CH}$, is formed, which crystallises in colourless needles, melts at 191° , and is sparingly soluble in water.

5-Bromo-6-oxy-2-anilinopyrimidine, $\text{NH} \begin{smallmatrix} \text{C}(\text{NHPh})\cdot\text{N} \\ \text{CO} \text{---} \text{CBr} \end{smallmatrix} \text{CH}$, obtained by the action of aniline on 6-oxy-5-bromo-2-ethylthiopyrimidine, crystallises in colourless needles, melts and decomposes at 246° , and is sparingly soluble in water, alcohol, benzene, or acetone; when this substance is heated with phosphorus oxychloride, 6-chloro-5-bromo-2-anilinopyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{NHPh})\cdot\text{N} \\ \text{CCl} \text{---} \text{CBr} \end{smallmatrix} \text{CH}$, is produced, which crystallises in long, radiating, colourless needles, melts at $106\text{--}107^{\circ}$, is readily soluble in ether or benzene, and is converted by aniline into 5-bromo-2:6-dianilinopyrimidine.

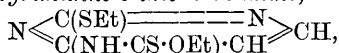
6-Oxy-2-ethylthiol-4-ethylpyrimidine, $\text{NH} \begin{smallmatrix} \text{C}(\text{SEt})\cdot\text{N} \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CEt}$ crystallises in colourless, transparent prisms, melts at 89° , and is very soluble in alcohol and slightly so in hot water; when this substance is treated with bromine, it is converted into 5-bromo-6-oxy-2-ethylthiol-4-ethylpyrimidine, $\text{NH} \begin{smallmatrix} \text{C}(\text{SEt})\cdot\text{N} \\ \text{CO} \text{---} \text{CBr} \end{smallmatrix} \text{CEt}$, which crystallises from alcohol in colourless, transparent prisms and melts at $172\text{--}173.5^{\circ}$. By the action of hot concentrated hydrochloric acid on 6-oxy-2-ethylthiol-4-ethylpyrimidine or its bromo-derivative, 4-ethyluracil, $\text{NH} \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{CH} \end{smallmatrix} \text{CEt}$, is obtained, which crystallises from alcohol in colourless tables, melts at 204° , effervesces at about 270° , and is readily soluble in water. 5-Bromo-4-ethyluracil, $\text{NH} \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{CBr} \end{smallmatrix} \text{CEt}$, crystallises in prisms or plates, melts at $230\text{--}231^{\circ}$, and is slightly soluble in hot water.

6-Oxy-2-methylthiopyrimidine hydrochloride melts and decomposes at 189° , and when warmed with a mixture of phosphorus pentachloride and phosphorus oxychloride is converted into 6-chloro-2-methylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{SMe})\cdot\text{N} \\ \text{CCl} \text{---} \text{CH} \end{smallmatrix} \text{CH}$, which is obtained as a colourless oil boiling at $139\text{--}140^{\circ}$ under 36 mm. pressure; it solidifies on cooling and melts at from -2° to -0° . When this chloro-derivative is heated with alcoholic ammonia, 6-amino-2-methylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{SMe})=\text{N} \\ \text{C}(\text{NH}_2)\cdot\text{CH} \end{smallmatrix} \text{CH}$, is formed, which crystallises in colourless, prismatic plates, melts at $125\text{--}126^{\circ}$, and is readily soluble in alcohol or acetone. E. G.

Pyrimidines: Action of Potassium Thiocyanate on Certain Imide Chlorides. IX. HENRY L. WHEELER and H. STANLEY BRISTOL (*Amer. Chem. J.*, 1905, 33, 448—460).—2-Ethylthiol-6-thiocarbimidopyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt})=\text{N} \\ \text{C}(\text{NCS})\cdot\text{CH} \end{smallmatrix} \text{CH}$, obtained by the action of potassium thiocyanate on a solution of 6-chloro-2-ethylthiopyrimidine

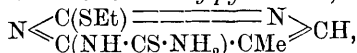
in toluene, boils at 180° under 32 mm. pressure, solidifies on cooling, crystallises from benzene in pale yellow, prismatic plates, and melts at 175°. When this compound is treated with ammonia, 2-ethylthiol-6-thiocarbamidopyrimidine, $\text{N} \begin{smallmatrix} \text{C(SEt)} \\ \text{C(NH}\cdot\text{CS}\cdot\text{NH}_2) \end{smallmatrix} \text{N} \text{CH} \text{CH}$, is produced, which crystallises from alcohol in long, thin, colourless prisms, melts at 214°, and is sparingly soluble in water. By the action of aniline on 2-ethylthiol-6-thiocarbimidopyrimidine, 2-ethylthiol-6-phenylthiocarbamidopyrimidine is formed, which crystallises in long, colourless needles, melts at 205°, and is fairly soluble in hot alcohol, but almost insoluble in hot water.

Ethyl 2-ethylthiolpyrimidine-6-thioncarbamate,

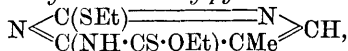


obtained by the action of an alcoholic solution of potassium thiocyanate on 6-chloro-2-ethylthiolpyrimidine, crystallises in long, thin, light yellow plates, melts at 93°, is readily soluble in hot alcohol, and is decomposed by hot concentrated hydrochloric acid with formation of uracil and cytosine.

2-Ethylthiol-6-thiocarbamido-5-methylpyrimidine,



obtained by the action of potassium thiocyanate on 6-chloro-2-ethylthiol-5-methylpyrimidine in presence of toluene, crystallises in radiating needles, melts at 192°, and is fairly soluble in hot alcohol or benzene and sparingly so in hot water. When the reaction mixture is boiled with alcohol, ethyl 2-ethylthiol-5-methylpyrimidine-6-thioncarbamate,

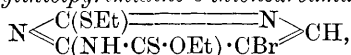


is produced, which crystallises in pale yellow prisms, melts at 88—89°, and is readily soluble in alcohol, ether, or benzene and sparingly so in water.

6-Chloro-5-bromo-2-ethylthiolpyrimidine (Wheeler and Johnson, Abstr., 1904, i, 624) boils at 168° under 24—25 mm. and at 179—180° under 36 mm. pressure. By the action of potassium thiocyanate on a solution of this substance in toluene, 5-bromo-2-ethylthiol-6-thiocarbimidopyrimidine, $\text{N} \begin{smallmatrix} \text{C(SEt)} \\ \text{C(NCS)} \end{smallmatrix} \text{N} \text{CH} \text{CH}$, is formed, which crystallises in small, pale yellow prisms, melts at 79—80°, and is readily soluble in benzene or toluene and sparingly so in light petroleum. If alcoholic ammonia is added to the reaction mixture, 5-bromo-2-ethylthiol-6-thiocarbamidopyrimidine separates, which crystallises in light yellow plates, melts at 220°, and is sparingly soluble in water or alcohol, but more soluble in benzene. When the thiocarbimide compound is treated with aniline, 5-bromo-2-ethylthiol-6-phenylthiocarbamidopyrimidine is obtained, which crystallises from alcohol in slender, colourless needles, melts at 166—167°, and is fairly soluble in benzene.

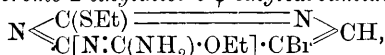
When 6-chloro-5-bromo-2-ethylthiolpyrimidine is heated with an alcoholic solution of potassium thiocyanate, ethyl 5-bromo-2-ethylthiolpyrimidine-6-thioncarbamate is produced, together with 5-bromo-6-thio-2-ethylthiolpyrimidine and 5-bromo-6-amino-2-ethylthiolpyrimidine.

Ethyl 5-bromo-2-ethylthiopyrimidine-6-thioncarbamate,



crystallises in long, pointed, light yellow, prismatic plates, melts at 82° , and is readily soluble in hot alcohol. *5-Bromo-6-thio-2-ethylthiopyrimidine*, $\text{NH} \begin{array}{c} \diagup \text{C(SET)} \cdot \text{N} \\ \diagdown \text{CS} \text{---} \text{CBr} \end{array} \text{CH}$, forms pale yellow plates, and melts

and decomposes at 198° ; this compound can also be prepared by the action of potassium hydrogen sulphide on 6-chloro-5-bromo-2-ethylthiopyrimidine. When ethyl 5-bromo-2-ethylthiopyrimidine-6-thioncarbamate is treated with ethyl bromide in presence of sodium ethoxide, *ethyl 5-bromo-2-ethylthiopyrimidine-6-iminothiocarbonate*, $\text{N} \begin{array}{c} \diagup \text{C(SET)} \\ \diagdown \text{C[N:C(SET) \cdot OEt]} \cdot \text{CBr} \end{array} \text{N} \text{---} \text{CH}$, is formed, which crystallises in long, colourless prisms, melts at 43° , and is readily soluble in alcohol or ether; if ammonia is passed into an alcoholic solution of this compound, *5-bromo-2-ethylthiol-6-ψ-ethylcarbamidopyrimidine*,



is obtained, which crystallises from alcohol in long needles, melts at 110° , decomposes at 230° , is readily soluble in benzene or warm alcohol, and sparingly so in hot water. When a solution of this ψ-carbamidopyrimidine in benzene is heated with sodium, *5-bromo-2-ethylthiol-6-cyanoamidopyrimidine* is produced. This compound is converted by concentrated hydrochloric acid into *5-bromo-2-ethylthiol-6-carbamidopyrimidine*, $\text{N} \begin{array}{c} \diagup \text{C(SET)} \\ \diagdown \text{C(NH} \cdot \text{CO} \cdot \text{NH}_2\text{)} \cdot \text{CBr} \end{array} \text{N} \text{---} \text{CH}$, which crystallises from alcohol and melts at 167° ; if the carbamidopyrimidine is heated at $170\text{--}180^\circ$, 5-bromo-6-amino-2-ethylthiopyrimidine is formed, whilst by the action of boiling concentrated hydrochloric acid it is converted into 5-bromocytosine (Abstr., 1904, i, 625).

2-Thiouracil, $\text{NH} \begin{array}{c} \diagup \text{CS} \cdot \text{NH} \\ \diagdown \text{CO} \text{---} \text{CH} \end{array} \text{CH}$, obtained by the action of ethyl sodioformylacetate on thiocarbamide, crystallises in colourless prisms and decomposes above 300° .

6-Anilino-2-ethylthiopyrimidine hydrochloride, produced by the action of aniline on 6-chloro-2-ethylthiopyrimidine, melts and decomposes at 198° ; the corresponding *base* crystallises in colourless needles, melts at 68° , and is very soluble in alcohol. When the hydrochloride is boiled with strong hydrochloric acid, *2-oxy-6-anilinopyrimidine (phenylcytosine) hydrochloride*, $\text{N} \begin{array}{c} \diagup \text{CO} \text{---} \text{NH} \\ \diagdown \text{C(NHPh)} \cdot \text{CH} \end{array} \text{N} \text{---} \text{CH} \cdot \text{HCl}$, is obtained, which decomposes at 228° ; the *base* crystallises in colourless, six-sided plates, melts at about 269° , and is fairly soluble in hot alcohol; the *platinichloride* crystallises with $1\text{H}_2\text{O}$.

2:6-Dianilinopyrimidine, $\text{N} \begin{array}{c} \diagup \text{C(NHPh)} = \text{N} \\ \diagdown \text{C(NHPh)} \cdot \text{CH} \end{array} \text{CH}$, prepared by heating 6-chloro-2-ethylthiopyrimidine (1 mol.) with aniline (2 mols.), crystallises from alcohol in six-sided plates, melts at $136\text{--}137^\circ$, and is fairly soluble in hot benzene or ether; the *hydrochloride* melts at 197° .

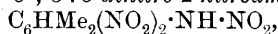
2-Ethylthiol-5-phenyluracil, $\text{NH} \begin{array}{c} \diagup \text{C(SET)} \cdot \text{N} \\ \diagdown \text{CO} \text{---} \text{CPh} \end{array} \text{CH}$, obtained by the

condensation of sodium phenylformylethylacetate with the additive compound of thiocarbamide with ethyl iodide, crystallises in long needles, melts at 158° , and is readily soluble in alcohol or hot water. When this compound is heated with concentrated hydrochloric acid, it is converted into 5-phenyluracil, $\text{NH} \begin{smallmatrix} \text{CO-NH} \\ \text{CO-CPh} \end{smallmatrix} \text{CH}$, which forms microscopic plates and does not melt below 350° . E. G.

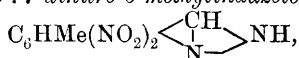
Action of Nitric Acid on Aminosulphonic Acids; Nitroamines, Diazo-compounds, and Indazoles. THEODOR ZINCKE (*Annalen*, 1905, **339**, 202—241).—Although the action of nitric acid on aminosulphonic acids has been investigated, so far only nitrodiazobenzenesulphonic acids have been observed as the products of the reaction. It has been found that *m*-aminobenzenesulphonic acids yield nitrodiazobenzenesulphonic acids, whilst the *o*- and *p*-aminobenzenesulphonic acids yield nitrated nitroaminobenzenes together with diazo-salts. In the case of the two classes of compounds last mentioned, the sulphonic groups are first replaced by nitro-groups, and these stable nitroanilines then converted into nitroamines. In the *m*-compounds, the sulphonic acid group is not replaced, and consequently oxidation takes place, nitrous acid is formed, and then the amine converted into diazo-compound.

When a methyl group is in the ortho-position with respect to the nitroamino-group, indazoles are formed.

[With E. ELLENBERGER.]—When *p*-xylidinesulphonic acid is added to pure nitric acid at -5° , 3 : 5-dinitro-2-nitroamino-*p*-xylene,



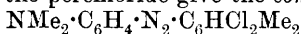
is obtained as colourless needles melting and decomposing at 130° ; when boiled with phenol, it is converted into the corresponding dinitro-xylidine; the potassium, sodium, and silver salts form needles. By nitrous acid, the nitroamine is converted into the nitrodiazo-xylene, which is also formed as a by-product in the action of the nitric acid on the sulphonic acid; the diazo-compound forms a coupled product with dimethylaniline, $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_5$, which crystallises in reddish-brown leaflets melting at 220° ; a perbromide was prepared. When boiled in aqueous solution, 5 : 7-dinitro-6-methylindazole,



is obtained as colourless needles melting at 228° ; it is also formed directly from the sulphonic acid by diluting with water after treatment with nitric acid and boiling; the sodium salt crystallises in reddish-yellow needles, and the silver salt is a pale yellow, crystalline powder. The acetyl compound crystallises in plates melting at 185° .

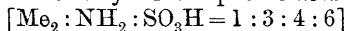
3 : 5-Dichloro-*p*-xylene-2-diazonium perchloride, $\text{C}_6\text{HCl}_2\text{Me}_2 \cdot \text{N}_2\text{Cl}_3$, is obtained when a solution of the nitroamine in acetyl chloride or chloroform is treated with chlorine, and crystallises in leaflets or needles melting at 120° ; by treatment with potassium bromide, the perbromide is formed, crystallising in pale yellow needles decomposing at 155° . The platinichloride, $\text{C}_{16}\text{H}_{14}\text{N}_4\text{Cl}_6 \cdot \text{PtCl}_4$, forms pale yellowish-brown leaflets melting and decomposing at 159° . Very explosive per-

manganates and perchlorates can be prepared from the perchloride. Dimethylaniline and the perchloride give the compound



as orange-red needles melting at 121° ; the β -naphthol derivative crystallises in red needles melting at 195° .

[With A. MAUÉ.]—The *m*-xylidinesulphonic acid



and nitric acid yield, not a nitroamine but 2-nitro-4-diazo-xylene-6-sulphonic acid, which crystallises in needles exploding on heating; with dimethylaniline it yields a dimethylaniline salt of a dimethylanilineazonitro-xylenesulphonic acid, which crystallises in red needles unchanged at 200° ; the ammonium salt forms dark red needles. The free acid crystallises in reddish-yellow needles unchanged at 250° . The β -naphthylamine salt of the naphthylamineazonitro-xylenesulphonic acid crystallises in deep red needles, and the ammonium in red needles. The free acid forms dark red needles.

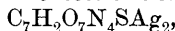
[With PH. MALKOMESIUS.]—The main product of the action of nitric acid on *o*-toluidine-5-sulphonic acid is 3 : 5-dinitro-2-nitroaminotoluene, which forms yellow, explosive crystals melting at 92° . The sodium salt crystallises in yellow leaflets or needles, the barium salt in yellow leaflets, and the silver salt is a yellow, crystalline powder. With nitrous acid, the nitroamine yields a diazo-compound, with tin and hydrochloric acid a triaminotoluene, with chlorine and acetyl chloride a chlorinated diazo-compound, and with bleaching powder a tetranitroazotoluene. The sodium salt of the nitroamine and methyl iodide yield the *N*-methyl ester, which forms brass-yellow crystals melting at 119° ; the *O*-ester is obtained from the silver salt, and crystallises in yellow plates melting at $72\text{--}73^\circ$. Phenol converts the nitroamine into 3 : 5-dinitro-*o*-toluidine. 2 : 4 : 2' : 4'-Tetranitro-*o*-azotoluene is formed when bleaching powder solution is added to a solution of the sodium salt of the nitroamine in methyl alcohol and acetic acid added; it crystallises in yellowish-red needles melting and decomposing at 218° . 3 : 5-Dinitrotoluene-2-diazonium nitrate is obtained as a by-product in the preparation of the nitroamine, and is converted into a β -naphthylamine derivative, which crystallises in reddish-brown needles melting at 117° ; the perbromide is a pale red, crystalline powder exploding at 64° . With ammonia it yields 3 : 5-dinitrotoluene-diazoimide, and, when boiled with alcohol, 2-bromo-3 : 5-dinitrotoluene, which forms yellow crystals melting at $91\text{--}92^\circ$. 5 : 7-

Dinitroindazole, $\begin{array}{c} \text{C}(\text{NO}_2) \cdot \text{CH} : \text{C} \cdot \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{N} \end{array} \text{---} \text{NH}$, prepared by boiling an aqueous solution of the diazonium salt, crystallises in yellow needles melting at 215° ; the sodium salt forms yellowish-red needles; the silver salt is a yellow, crystalline precipitate, and the acetyl derivative forms yellow needles melting at 196° .

[With A. KUCHENBECKER.]—At a low temperature, sulphanilic acid gives 2 : 4-dinitroaniline and at a higher temperature diazobenzene-*p*-sulphonic acid. 2 : 6-Dibromosulphanilic acid yields 2 : 6-dibromo-4-nitro-1-nitroaminobenzene, a greyish-white, crystalline powder, exploding on heating. 2 : 4-Dinitro-1-nitroaminobenzene is formed from *o*-nitrosulphanilic acid at -15° and is a colourless, crystalline powder

melting and decomposing at 101° . *p*-Toluidine-5-sulphonic acid yields 3:5-dinitro-4-nitroaminotoluene, which forms colourless crystals melting and decomposing at 104° . The silver salt forms brass-yellow crystals.

m-Sulphanilic acid is converted by nitric acid into 3-nitrodiazobenzene-5-sulphonic acid, $\text{NO}_2 \cdot \text{C} \begin{array}{l} \text{CH} \cdot \text{C} - \text{SO}_2 \\ \text{CH} : \text{C} - \text{N}_2 \end{array} \text{O}$, which is a yellowish-white powder exploding on heating. Similarly, 2:6-dibromo-*m*-sulphanilic acid yields 2:6-dibromo-3-nitrodiazobenzene-5-sulphonic acid, a yellow, explosive, crystalline powder. From *p*-toluidine-6-sulphonic acid, 2-nitro-*p*-diazotoluene-6-sulphonic acid is obtained as thick, yellow, explosive crystals. *o*-Toluidine-4-sulphonic acid yields 3:5-dinitro-*o*-diazotoluene-4-sulphonic acid, which forms colourless crystals becoming brown in the air and exploding on heating. When boiled with acids, it passes into 5:7-dinitroindazole-6-sulphonic acid, which crystallises in colourless needles; the silver salt, $\text{C}_7\text{H}_5\text{O}_7\text{N}_4\text{SAg} \cdot \text{H}_2\text{O}$, crystallises in yellow plates and yields with excess of silver nitrate the salt



which is a brass-yellow, crystalline powder. The potassium and ammonium salts crystallise with $2\text{H}_2\text{O}$ in colourless needles. When the sodium salt is heated with concentrated sodium hydroxide, 5:7-dinitro-6-hydroxyindazole, $\text{C}_7\text{H}_4\text{O}_5\text{N}_4$, is formed as brass-yellow needles melting at $232\text{--}233^{\circ}$; with sodium carbonate, it yields a phenolic sodium salt, which is yellow, and with sodium hydroxide the disodium salt, which is deep red, but hydrolysed by water into the yellow salt. Ammonia gives only one salt. The diacetyl derivative, $\text{C}_{11}\text{H}_8\text{O}_7\text{N}_4$, crystallises in needles melting at 195° . When boiled with ammonia, 5:7-dinitro-6-aminoindazole is formed, and crystallises in brownish-yellow scales melting above 270° . The diacetyl compound crystallises in needles melting and decomposing at 182° . Aniline converts the indazolesulphonic acid into 5:7-dinitro-6-anilinoindazole, $\text{C}_{13}\text{H}_9\text{O}_4\text{N}_5$, which forms red crystals; other bases yield similar compounds.

K. J. P. O.

Condensation of Flavinduline with Methylene Compounds.

II. FRANZ SACHS and GUIDO BARGELLINI (*Ber.*, 1905, 38, 1742—1745. Compare Abstr., 1899, i, 239).—Flavinduline hydrobromide condenses with ethyl acetoacetate in alcoholic solution in the presence of sodium hydroxide to form the compound $\text{C}_{32}\text{H}_{24}\text{O}_5\text{N}_2$, which separates from a mixture of benzene and light petroleum as a dark blue powder and melts at $205\text{--}206^{\circ}$. Its solution in acetic acid is orange-red, and with nitric acid it forms a dark red oil. When hydrogen chloride is passed into the solution of the condensation product in toluene, a violet-red powder separates from the alcoholic solution, of which the platinichloride, $\text{C}_{64}\text{H}_{50}\text{O}_4\text{N}_4\text{Cl}_6\text{Pt}$, was prepared.

The condensation product, $\text{C}_{34}\text{H}_{21}\text{N}_3$, prepared from flavinduline and benzyl cyanide, forms dark green crystals and melts at $240\text{--}241^{\circ}$. With glacial acetic acid it forms a green solution, and with concentrated sulphuric acid a cherry-red solution.

The condensation product, $\text{C}_{31}\text{H}_{22}\text{O}_2\text{N}_2$, formed from flavinduline and

acetylacetone, is an olive-green powder and melts at 240—245°. Its solution in acetic acid is brownish-yellow. Its solution in concentrated sulphuric acid is cherry-red.

The condensation *product*, $C_{33}H_{26}O_4N_2$, prepared from flavinduline and ethyl malonate, forms dark green crystals with a violet lustre. With alcohol, glacial acetic acid, and concentrated sulphuric acid respectively, its solutions are greenish-blue, olive-green, and cherry-red respectively.

The condensation *product*, $C_{31}H_{21}O_2N_3$, prepared from flavinduline and ethyl cyanoacetate, forms dark green crystals with a violet lustre. It forms a bluish-green solution with ethyl alcohol and glacial acetic acid respectively, whilst its solution in concentrated sulphuric acid is red.

The condensation *product*, $C_{29}H_{16}N_4$, prepared from flavinduline and malononitrile, forms dark green crystals with a violet lustre. Its solution in glacial acetic acid is green, and in concentrated sulphuric acid red.

A. McK.

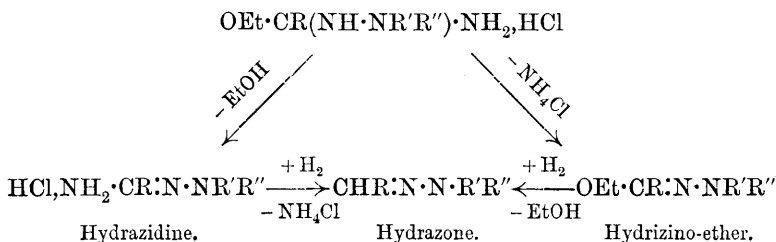
Condensation of Formisobutaldol with Dimethylaniline. MAXIMILIAN SAMEC (*Monatsh.*, 1905, 26, 391—411. Compare Wessely, *Abstr.*, 1900, i, 428).—When heated together with zinc chloride at 130°, formisobutaldol and dimethylaniline react yielding the *leuco-base*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot CMe_2 \cdot CH(C_6H_4 \cdot NMe_2)_2$, which forms colourless crystals, melts at 94—95°, or sometimes at 85°, is easily soluble in alcohol, ether, benzene, light petroleum, or dilute acids, and forms crystalline salts; the *oxalate* and the *hydrochloride* are colourless; the *platinichloride* is brown. On oxidation of the leuco-base with lead peroxide, the carbinol and its anhydride are formed; these are precipitated with zinc chloride and treated with ammonia, when the *carbinol*, $C_{29}H_{39}ON_3$, is obtained in colourless crystals. On warming, or in a vacuum at the laboratory temperature, this loses water and forms the *anhydride*, $C_{29}H_{37}N_3$, as a brittle, blue mass, which is reduced by zinc and hydrochloric acid to the leuco-base. The *oxalate*, $C_{29}H_{37}N_3 \cdot 3C_2H_2O_4$, is hygroscopic; the *zincchloride*, $C_{29}H_{37}N_3 \cdot 2ZnCl_2$, dyes animal fibres directly, vegetable fibres when mordanted; the *tetrahydrochloride*, $C_{29}H_{37}N_3 \cdot 4HCl$, is hygroscopic, softens at 55°, gradually evolves hydrogen chloride, and melts at 101—103°; the green *trihydrochloride*, $C_{29}H_{37}N_3 \cdot 3HCl$, melts at about 150°. When fused, the dye and its salts are dark blue with red fluorescence; the alcoholic solution of the dye and the very dilute aqueous or moderately dilute alcoholic solutions of the salts are reddish-blue, whilst the concentrated aqueous or moderately acid solutions of the salts are green. The differences have been studied spectrophotometrically and the results expressed in curves typical of the different states. Measurements of the electrical conductivity of solutions of various concentrations of the trihydrochloride show that the change from green to blue on dilution is accompanied by a change in the molecular conductivity.

When heated with sodium ethoxide in absolute alcoholic solution, the tetrahydrochloride of the dye forms the *ethyl ether* of the carbinol, $C_{29}H_{35}N_3 \cdot OEt$, which separates in scarlet crystals and melts at 65°.

On treatment with aqueous potassium hydroxide, the salts of the dye are gradually converted into the carbinol; the velocity of the change can be measured by the diminution of the electrical conductivity of the solution.

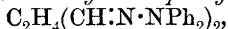
G. Y.

Reduction of Derivatives of Carboxylic Acids to Derivatives of Aldehydes. II. FRANZ HENLE (*Ber.*, 1905, 38, 1362—1369).—The reduction of imino-ethers dissolved in a mineral acid by sodium amalgam in presence of phenylhydrazine or a similar substance (*Abstr.* 1902, i, 790) probably occurs through the intermediate formation of an additive compound, thus:



Using acetic acid in the reduction in place of a mineral acid, a hydrizino-ether separates. The bases available for the reduction are semicarbazide, phenylhydrazine (not in all cases), phenylmethyl-, diphenyl-, and phenylbenzyl-hydrazines. The following do not give a favourable result: piperyl- and benzyl-hydrazines, aniline, *p*-toluidine, mesidine, α -naphthylamine, *ac*-tetrahydro- β -naphthylamine, benzidine. Sodium amalgam cannot be replaced by any other reducing agent.

The following reductions are described: *p*-tolimino-ether to *p*-tolualdehyde phenylhydrazone; phenylacetimino-ether to phenylacetaldehydephenylhydrazone and the following derivatives: (1) *phenylacetaldehydediphenylhydrazone*, $\text{CH}_2\text{Ph} \cdot \text{CH} : \text{N} \cdot \text{NPh}_2$, separates from alcohol in colourless crystals and melts at 101—102°; (2) *phenylacetaldehydphenylbenzylhydrazone* crystallises from alcohol in colourless needles and melts at 80—81°; (3) *phenylacetaldehydesemicarbazone* separates from ethyl acetate as a heavy, white, crystalline powder and melts at 156°. Succinimino-ether gives the following substances with different hydrazines: *succinaldehydebisdiphenylhydrazone*,



crystallises from alcohol in long, colourless needles and melts at 120°; *succinaldehydebisphenylmethylhydrazone*, $\text{C}_2\text{H}_4(\text{CH} : \text{N} \cdot \text{NMePh})_2$, crystallises from light petroleum in colourless prisms and melts at 86°; *succinaldehydebisphenylbenzylhydrazone* crystallises from light petroleum and melts at 147—148°.

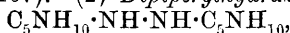
Phenylacetophenylhydrizinoether, $\text{CH}_2\text{Ph} \cdot \text{C}(\text{OEt}) : \text{N} \cdot \text{NHPh}$, is prepared from phenylacetimino-ether hydrochloride by treatment with magnesium powder and phenylhydrazine in cold 4 per cent. acetic acid solution; it crystallises from heavy petroleum in long, colourless needles, melts at 76°, and when distilled with steam after adding oxalic acid gives ethyl phenylacetate.

W. A. D.

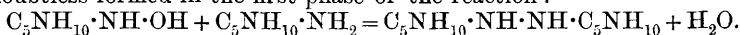
Hydroxydiphenyltriazine and Hydroxydiphenyldihydrotriazine. HEINRICH BILTZ (*Ber.*, 1905, **38**, 1417—1419).—3-Hydroxy-5:6-diphenyl-1:2:4-triazine (Thiele, *Abstr.*, 1895, i, 251) is best prepared by the interaction of benzil and semicarbazide hydrochloride in glacial acetic acid solution; it boils at 224—225°. The corresponding *hydroxy-triazine* derivative from anisil melts at 261—262°, that from piperil at 248°, and that from cumiril at 250°. *Hydroxydiphenyldihydrotriazine*, prepared by the reduction of the foregoing compound with zinc shavings and acetic acid, crystallises in colourless needles and melts at 275—276°. The corresponding *dihydro*-compound from anisil melts at 212—213°, that from piperil at 285°, and that from cumiril at 255—256°. E. F. A.

A Reaction of Secondary Amines. ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 272—277. Compare Angeli, *Abstr.*, 1901, i, 57, and Angeli and Angelico, *Abstr.*, 1901, i, 322).—It has been shown (*loc. cit.*) that nitroxyl, which is probably an anhydride of dihydroxyammonia, readily reacts with secondary amines, NHR^1R^2 , giving rise to tetrazones when R and R¹ are aliphatic residues or to diazo-compounds when R is an aromatic group and R¹ hydroxyl.

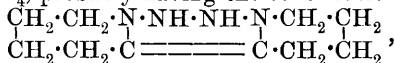
When molecular proportions of piperidine hydrochloride and sodium nitrohydroxylamine are heated together in concentrated aqueous solution, the following compounds are formed: (1) the piperylhydrazine, $\text{C}_5\text{H}_{12}\text{N}_2$, obtained by Knorr by reducing the corresponding nitrosoamine (*Abstr.*, 1884, 467). (2) *Dipiperylhydrazine*,



which separates from water in large, colourless crystals melting at 98°, readily reduces Fehling's solution, and reacts with benzoyl chloride, potassium cyanate, and benzaldehyde. Its formation is probably due to the action of piperylhydrazine on the hydroxypiperylhydrazine doubtless formed in the first phase of the reaction:



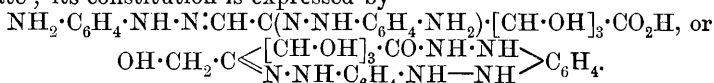
It yields a *picrate*, $(\text{C}_5\text{H}_{11}\text{N})_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, which crystallises from alcohol in yellow needles, melting and decomposing at 175°. (3) Piperyltetrazone, $\text{C}_{10}\text{H}_{10}\text{N}_4$, obtained by oxidising piperylhydrazine by means of mercuric oxide (*Abstr.*, 1882, 1115, and 1884, 467). (4) A compound, $\text{C}_{10}\text{H}_8\text{N}_4$, probably having the constitution



which separates from light petroleum in large, colourless crystals melting at 154°. It may be obtained in a purer state by oxidising the original mixture with mercuric oxide. It reduces Fehling's solution and yields a benzoyl derivative and a *picrate*, $\text{C}_{10}\text{H}_{18}\text{N}_4 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, melting at 174°. T. H. P.

Derivative of Glycuronic Acid and *p*-Nitrophenylhydrazine. AN. K. MEDVEDEFF (*Ber.*, 1905, **38**, 1646—1650).—The action of a solution of *p*-nitrophenylhydrazine on a solution of glycuronic acid, almost saturated with sodium acetate and rendered faintly alkaline with sodium carbonate, yields a compound, $\text{C}_{18}\text{H}_{22}\text{O}_5\text{N}_6$, which crystal-

lises from dilute alcohol in flat, monoclinic (?) prisms melting and decomposing at 125°. The compound is of the hydrazone-hydrazide or osazone type, and contains the *p*-nitrophenylhydrazine in a reduced state; its constitution is expressed by



It dissolves comparatively easily in the ordinary solvents, and also in solutions of acids and alkalis. Fehling's solution and ammoniacal silver solutions are reduced by it in the cold. If its alcoholic solution is heated with ferric chloride and the cooled liquid shaken with chloroform, the latter assumes an intense blood-red coloration, whilst the aqueous alcoholic layer becomes pale green. T. H. P.

5-Azoeugenol and its Constitution. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Gazzetta*, 1905, 35, i, 55—73).—When an alkaline solution of eugenol (1 mol.) is treated in the cold with the solution of a diazonium salt (1 mol.), precipitation of azoeugenol takes place immediately. The benzeneazo-, *m*-bromobenzeneazo-, and β -naphthaleneazo-compounds of eugenol, described in the present paper, behave towards alkalis like azophenols, and towards acetic anhydride like hydrazones of quinone, so that either of these constitutions may be ascribed to them.

Benzeneazoeugenol, $\text{OH} \cdot \text{C} \cdot \text{C}(\text{OMe}) : \text{CH}$
 $\text{N}_2\text{Ph} \cdot \text{C} - \text{CH} = \text{C} \cdot \text{C}_3\text{H}_5$, prepared by the ad-

dition of the diazo-solution obtained by the action of sodium nitrite on aniline (1 mol.) to an aqueous solution of eugenol (1 mol.) containing sodium hydroxide (2 mols.), crystallises from aqueous alcohol in long, dark red, silky needles, which melt at 75—76° (compare Borsche and Streitberger, *Abstr.*, 1904, i, 1064) and have the normal molecular weight in freezing benzene; it dissolves in dilute alkali solutions, giving an intense red coloration, reacts energetically with concentrated nitric acid, but is not dissolved by hydrochloric acid, although tin and hydrochloric acid or zinc and acetic acid convert it into aniline and amino-eugenol; it dissolves readily in alcohol, benzene, chloroform, acetone, or acetic acid, and to a less extent in ether or light petroleum; when crystallised from very dilute alcohol, it is obtained in yellow leaflets which melt at 79—80° and are probably hydrated, since an hour's heating at 60° converts them into the red needles melting at 75—76°. With bromine in chloroform solution, it yields the *dibromide*, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2\text{Br}_2$, which crystallises from a mixture of light petroleum and benzene, or from alcohol in golden-yellow scales melting at 98°. The *ethyl* derivative, $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$, forms a dark red, oily liquid boiling at 175° under 30 mm. pressure; it is soluble in dilute alkali solutions, and hence does not possess the character of an oxygen-ether. Benzeneazoeugenol does not undergo hydrolytic dissociation when boiled with hydrochloric acid or when its alcoholic solution is boiled with alkali hydroxide. It does not react with phenylhydrazine or hydroxylamine, but combines with 1 mol. of hydrogen chloride forming an unstable *hydrochloride*, which is obtained in long, white crystals melting at about 75°. The *acetyl* derivative, $\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2$, separates from light

petroleum in orange-red, acicular crystals, melts at 65° , and dissolves readily in alcohol, ether, benzene, or chloroform; when boiled with alcoholic hydrogen chloride, it is converted into benzeneazoeugenol, whilst zinc and acetic acid transform it into acetanilide and amino-eugenol, so that the acetyl group must be united to nitrogen, thus:

$$\text{NPhAc} \cdot \text{N} : \text{C} \begin{array}{l} \text{CH} : \text{C}(\text{C}_3\text{H}_5) \\ \text{CO} : \text{C}(\text{OMe}) \end{array} \text{CH}.$$

m-Bromobenzeneazoeugenol, $\text{C}_6\text{H}_4\text{Br} \cdot \text{N}_2 \cdot \text{C} \begin{array}{l} \text{C}(\text{OH}) \cdot \text{C}(\text{OMe}) \\ \text{CH} = \text{C}(\text{C}_3\text{H}_5) \end{array} \text{CH}$,

prepared in similar manner to benzeneazoeugenol, separates from light petroleum as a dark red, crystalline powder melting at 100° , and is moderately soluble in all the common organic solvents; its colour is somewhat intensified by dilute alkali hydroxide solution, and after boiling with sodium ethoxide in alcoholic solution the addition of water precipitates a voluminous, yellow compound melting at 96° ; it is soluble in concentrated sulphuric acid with formation of a dark red coloration, and reacts with fuming nitric acid so energetically that it ignites; it does not react with phenylhydrazine or hydroxylamine; the *acetyl* derivative, $\text{C}_{18}\text{H}_{17}\text{O}_5\text{N}_2\text{Br}$, separates from alcohol in orange-coloured, prismatic needles melting at 92 – 93° and soluble in the more common organic solvents, and is converted into *m*-bromobenzeneazoeugenol and ethyl acetate by boiling its alcoholic solution with hydrochloric acid.

β -Naphthaleneazoeugenol, $\text{C}_{10}\text{H}_7 \cdot \text{N}_2 \cdot \text{C} \begin{array}{l} \text{C}(\text{OH}) \cdot \text{C}(\text{OMe}) \\ \text{CH} = \text{C}(\text{C}_3\text{H}_5) \end{array} \text{CH}$, crystallises from alcohol in small, nearly black, prismatic needles, which give a brick-red powder, melts at 102° , and is soluble in the more common organic solvents; it dissolves in concentrated sulphuric acid, giving a reddish-brown coloration, and reacts energetically with fuming nitric acid; it does not react with phenylhydrazine or hydroxylamine, but yields an unstable, crystalline *hydrochloride*, and, on reduction with tin and hydrochloric acid, gives amino-eugenol; the *sodium* derivative, $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_2\text{Na}$, forms an intense carmine-red, crystalline precipitate, melting and decomposing at 233° , and is reconverted into β -naphthaleneazoeugenol by dilute hydrochloric acid; the *acetyl* derivative, $\text{C}_{10}\text{H}_7 \cdot \text{NAc} \cdot \text{N} : \text{C} \begin{array}{l} \text{CH} : \text{C}(\text{C}_3\text{H}_5) \\ \text{CO} : \text{C}(\text{OMe}) \end{array} \text{CH}$, crystallises from alcohol in red needles melting at 108° and soluble in benzene or light petroleum, and, on reduction with zinc and acetic acid, yields aceto- β -naphthalide and amino-eugenol. T. H. P.

Action of Diazonium Compounds on Malonic Acid.

MAX BUSCH and WILH. WOLBRING (*J. pr. Chem.*, 1905, [ii], 71, 366–381. Compare Abstr., 1903, i, 537).—*o*-Nitrophenyldiazonium acetate reacts with malonic acid, yielding di-*o*-nitroformazyl and the *o*-nitrophenylhydrazone of glyoxylic acid.

Di-o-nitroformazyl, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, crystallises in dark red needles and melts at 186 – 187° . The *ammonium* salt, $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} : \text{N} : \text{CH} \cdot \text{CO}_2\text{H})_2\text{NH}_3$, crystallises in orange needles and melts and decomposes at 197 – 198° . The *silver* salt, $\text{C}_8\text{H}_6\text{O}_4\text{N}_3\text{Ag}$, crystallises in grey needles; the *sodium* salt forms needles; the

methyl ester crystallises in yellow, glistening needles and melts at 140° ; the *ethyl* ester forms yellow needles and melts at 106° .

p-Nitrophenyldiazonium acetate reacts with malonic acid, forming *di-p*-nitroformazyl, as a brown, crystalline powder, and the *p*-nitrophenylhydrazone of glyoxylic acid. The ammonium salt, $C_{16}H_{17}O_8N_7$, forms a yellow, crystalline mass, which commences to sinter at 190° and melts and decomposes at 250° .

The action of *m*-nitrophenyldiazonium acetate on malonic acid leads to the formation of the formazyl compound only.

o-Bromophenyldiazonium acetate reacts with malonic acid to form the *o*-bromophenylhydrazone of glyoxylic acid, which crystallises in yellow needles and melts at 156° . *p*-Bromophenyldiazonium acetate and malonic acid yield *di-p*-bromoformazyl, which forms dark red, crystalline aggregates and melts at 114 — 115° .

The *o*-iodophenylhydrazone of glyoxylic acid crystallises in glistening, yellow leaflets and melts and decomposes at 160° . *Di-o*-iodoformazyl crystallises in glistening, red needles and melts and decomposes at 168 — 169° .

The action of *o*-chlorophenyldiazonium acetate and sodium nitrite on malonic acid leads to the formation of *o*-chlorophenylazoformaldoxime, $C_6H_4Cl \cdot N : N \cdot CH : N \cdot OH$, which crystallises in glistening, orange needles, melts at 150° , and is reduced by zinc dust or ammonium sulphide in alcoholic solution to *o*-chlorophenylhydrazoformaldoxime; this crystallises in glistening, white leaflets, becomes red at 133° , melts and decomposes at 137° , and is easily oxidised to the azo-compound. When warmed with concentrated hydrochloric acid, *o*-chlorophenylazoformaldoxime gradually dissolves, and the solution deposits *o-p*-dichlorophenylhydrazoformaldoxime in colourless needles melting at 143° .

α -Naphthylazoformaldoxime crystallises in yellow, microscopic needles, or glistening, dark red needles, and melts and decomposes at 151 — 152° . *β* -Naphthylazoformaldoxime crystallises in small, yellow or long, red needles and melts at 155 — 156° . Phenylazoformaldoxime is formed by the action of phenyldiazonium acetate and sodium nitrite on malonic acid (compare Bamberger and Frei, Abstr., 1902, i, 404). *o*-Tolylazoformaldoxime is a reddish-yellow oil. *o*-Anisylazoformaldoxime crystallises in yellow needles and melts at 140 — 141° . *as-m*-Xylylazoformaldoxime, from *as-m*-xylyldiazonium acetate, malonic acid, and sodium nitrite, crystallises in slender, yellow needles and melts at 125° .

G. Y.

Action of Diazonium Compounds on Iminazoles. HERMANN PAULY (*Zeit. physiol. Chem.*, 1905, 44, 159, 160).—Polemical. A reply to Burian (*ibid.*, 43, 502).

J. J. S.

Secondary Diazoamino-compounds. LÉO VIGNON and ADOLPHE SIMONET (*Compt. rend.*, 1905, 140, 1038—1040. Compare this vol., i, 397).—Methylanilinoazobenzene, $NPh : N \cdot NMePh$, is obtained by adding an aqueous solution of diazobenzene chloride to an alcoholic solution of methylaniline, and separates in the form of a yellow oil on

adding excess of water. By the same method several other secondary diazoamino-compounds were obtained.

Ethylanilinoazobenzene, $\text{NPh:N}\cdot\text{NEtPh}$, forms an orange-yellow oil which partially solidifies after being kept for some time.

Benzylanilinoazobenzene, $\text{NPh:N}\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$, separates as a red oil which solidifies and melts at 74° .

Dibenzylaminoazobenzene, $\text{NPh:N}\cdot\text{N}(\text{CH}_2\text{Ph})_2$, crystallises in pale yellow needles melting at 83° .

Diethylaminoazobenzene, $\text{NPh:N}\cdot\text{NEt}_2$, separates in the form of a mobile, red liquid and boils at $258\text{--}260^\circ$.

Acids hydrolyse these diazoamino-compounds, yielding nitrogen, phenol, and the secondary amines.

H. M. D.

Adsorption Theory of the Neutralisation of Toxins and Related Phenomena. WILHELM BILTZ, H. MUCH, and C. SIEBERT (*Chem. Centr.*, 1905, i, 1107—1108; from *Behring's Beitr. exper. Therapie*, Heft 10).—The experiments indicate that all + colloids precipitate proteid solutions of various kinds; in general, - colloids do not bring about precipitation. The action of the various colloids on solutions of saponin leads to the same subdivision. Solutions of many specific proteid materials become less active when shaken up with various hydrogels. The hydroxide hydrogels have approximately the same effect on a given solution. If the concentration of the proteid is varied, the effect produced by a given quantity of hydrogel is relatively greater in the dilute solutions.

The diminution of the activity of the proteid solution cannot be explained on the assumption that the proteid is simply absorbed unchanged by the hydrogel, for unchanged active substance cannot be extracted from hydrogels which have been shaken up with proteid solutions. The effect of the colloids is rather to increase the rate of decomposition of the proteids. The authors regard the action as a "neutralisation phenomenon," which takes place in two stages. In the first, absorption of the active substance by the colloid takes place, and in the second the absorbed substance decomposes. The diminution of the activity of the solution is thus determined by the individual velocities of these consecutive changes.

H. M. D.

Separation of Proteids. H. C. HASLAM (*J. Physiol.*, 1905, 32, 267—290).—Attention is drawn to the inexactitude of various methods for the separation of proteids by precipitation, especially by neutral salts. The precipitate should be redissolved and again precipitated, and this repeated until the organic nitrogen in the filtrate is constant. When the proteid it is sought to purify is in the filtrate, other proteids being got rid of by precipitation, the treatment is more complicated, and a method of fractional precipitation, to be carefully distinguished from Pick's method of taking fractions, is described at length. The previous methods in use are quite inadequate to obtain pure substances. By the new methods it is shown that albumoses can be separated from peptones, and that there are three primary albumoses (hetero-, α -proto-, and β -proto-). Among other practical points, the

use of sodium sulphate at 37° is recommended instead of ammonium sulphate; the estimation of nitrogen in the filtrate is then simpler.

It is stated that, in the usual fractional method, each fraction contains every proteid in a mixture; the first fractions will naturally contain a large quantity of the most insoluble and a small quantity of the most soluble; the last fractions the reverse. The doctrine of natural boundaries in salting out leads to erroneous results. It is suggested that some sort of loose chemical combination existing between the proteids in a mixture will explain the tenacity with which they cling together.

W. D. H.

The Carbohydrate Group in Proteids. LEO LANGSTEIN (*Beitr. chem. Physiol. Path.*, 1905, 6, 349—357. Compare Abstr., 1903, i, 734).—The researches of previous workers on this question show great differences of opinion as to the character and amount of the carbohydrate group in proteids, some even denying that it exists at all in certain proteids. Among these investigations, the discovery of glucosyl-albumoses by Pick and Unger among the digestive products of egg-albumin is regarded as important. In the present research, the carbohydrate group in serum-albumin was found not in an albumose, but as a gluco-peptone in the ammonium sulphate filtrate. In regard to the globulin, the proteolytic experiments confirm the previous conclusion that several carbohydrates are obtainable, and that the carbohydrate group or groups are chemically combined with the original proteid, and not merely mechanically mixed. The fact that the blood proteids have such a composition is an important factor in the explanation of diabetes.

W. D. H.

Proteid Chemistry. EMIL ABDERHALDEN (*Chem. Centr.*, 1905, i, 884; from *Med. Klin.*, 1905, 1, Nos. 1 and 2).—The following simple products have been as yet obtained on hydrolysing proteids: glycine, alanine, aminovaleric acid, leucine, isoleucine, phenylalanine, glutamic acid, aspartic acid, cysteine, α -proline (pyrrolidine-2-carboxylic acid), hydroxy- α -proline, serine, tyrosine, tryptophan, lysine, arginine, histidine, diaminotrihydroxydodecoic, diaminoglutaric, diaminoadipic, amino-hydroxysuccinic, and diaminosuberic acids, an acid $C_9H_{16}O_7N_2$ (caseic acid), and an acid $C_{12}H_{24}O_5N_2$ (caseic acid).

The similarity of Fischer's synthetical polypeptides with the natural peptones is pointed out, and stress is laid on the importance of the action of the pancreas fragments on these polypeptides as throwing light on the different forms of linking of the amino-acids in the proteid molecule.

E. F. A.

Physical Alterations of Colloids. IV. Precipitation of Albumin by means of Salts of Heavy Metals. WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1905, 6, 233—259. Compare Abstr., 1902, ii, 388; 1903, i, 299; 1904, i, 356; Galeotti, *ibid.*, 1904, i, 355).—The precipitating action of solutions of the following salts of heavy metals on albumin solutions has been studied: cupric sulphate, cupric acetate, ferric chloride, ferric nitrate, zinc acetate, zinc chloride, lead acetate, silver nitrate, and mercuric chloride.

With zinc sulphate solutions, the precipitating action increases with the concentration of the sulphate from $0.001N$ to $0.05N$ for 20 per cent. albumin, then decreases, and finally disappears at a concentration between 1 and $2N$, but reappears again at higher concentrations. The precipitations with the more dilute solutions are non-reversible, whereas those with the concentrated solutions are reversible. With more concentrated albumin solutions, the precipitation is more copious, and the interval between non-reversible and reversible precipitation is smaller.

The phenomena of double precipitation maximum and difference of reversibility of the two maxima have not been observed with other readily soluble salts.

For a 10 per cent. albumin solution, the lowest concentration of cupric sulphate which produces precipitation is about 0.0008 — $0.001N$, but a normal solution does not produce precipitates nor even a $6N$ solution. With excess of albumin, the process is somewhat different (compare Galeotti, *loc. cit.*).

Silver nitrate represents a third type, and its precipitating action on 10 per cent. albumin is much the same with solutions varying from 0.1 — $6N$.

With horse serum diluted 100 times, and dialysed until its conductivity had fallen to that of distilled water, silver nitrate solutions varying from 0.1 to $2.0N$ gave no indication of a maximum, and also no signs of resolution of the precipitate.

The influence of salts of the alkali metals on the precipitating power of dilute ($0.005N$) solutions of zinc sulphate has been studied. All have an inhibiting influence, and this increases in the order SO_4'' , Cl' , $C_2H_3O_2'$, NO_3' , Br' , I' , SCN' for anions and K' , Na' , NH_4' , Mg'' for cations. With more concentrated zinc solutions ($4N$), the alkali salts have an intensifying action in the same order as given above for the anions. The phenomena observed here are very similar to those previously obtained by the addition of alkali salts to the alkali earth salts. The paper concludes with a chapter on the theory of albumin precipitation.

J. J. S.

Oxidation of Albumins. OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1905, 6, 296—328. Compare Maly, *Abstr.*, 1885, 824; 1889, 629; Löw, *ibid.*, 1885, 823; Bondzyński, *ibid.*, 1894, i, 479; Würster, *ibid.*, 1887, 607; Schulz, *ibid.*, 1900, i, 266; Bernert, *ibid.*, 1899, i, 315). —Maly's peroxyprotoic acid, obtained by oxidising casein with potassium permanganate in alkaline solution, is a mixture of at least three compounds of high molecular weight. These may be separated by fractional precipitation with silver nitrate, lead acetate, and mercuric acetate, and are termed A, B, and C peroxyprotoic acids. The compounds A and C do not differ materially from Maly's acid, whereas B contains much more oxygen and much less nitrogen.

The acids may readily be esterified by means of alcohol and hydrogen chloride. The *esters* are readily soluble in absolute alcohol or chloroform and are precipitated by the addition of ether to their chloroform solutions. They are hydrolysed by aqueous ammonia and appear to yield the unaltered acids. When boiled for several hours

with baryta water, the peroxyprotoic acids yield considerable quantities of barium oxalate and ammonia together with *diaminoprotoic acids*. These are biuret compounds which yield glutamic acid, benzoic acid, leucine, and ammonia on hydrolysis. Unlike the original peroxyprotoic acids, these diaminoprotoic acids are readily oxidised by alkaline permanganate at the ordinary temperature, yielding amorphous biuret derivatives—*Kyprotoic acids*—which, on hydrolysis, yield leucine, glutamic acid, oxalic acid, and ammonia.

The mean composition of the various compounds is :

	C.	H.	N.	O.	
Casein	53.0	7.0	15.7	22.65	per cent.
Maly's oxyprotosulphonic acid	51.21	6.89	14.59	25.54	„
Peroxyprotoic acid A and B	45.74	6.08	13.97	33.06	„
Kyprotoic acid A	43.24	6.42	11.08	38.68	„
Peroxyprotoic acid B	42.33	5.88	8.96	41.80	„

J. J. S.

Specific Rotation of Salts of Casein. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1905, 27, 363—366).—The following determinations were made at 20°. A solution made by dissolving 5 grams of casein in 45 c.c. of *N*/10 sodium hydroxide and diluting the product with water to 100 c.c. is neutral to phenolphthalein, and gives $[\alpha]_D - 103.5^\circ$ (based on the weight of casein). When only half this quantity of alkali is employed, $[\alpha]_D = -95.2^\circ$. A solution containing 5 grams of casein in 45 c.c. of *N*/10 potassium hydroxide, diluted with water to 100 c.c., gives $[\alpha]_D - 104.4^\circ$. A similar solution of casein in lithium hydroxide solution gives $[\alpha]_D - 100.8^\circ$, whilst a solution containing only 22.5 c.c. of *N*/10 lithium hydroxide gives $[\alpha]_D - 94.8^\circ$. The ammonium salt, made by dissolving 5 grams of casein in 45 c.c. of *N*/10 ammonia and diluting to 100 c.c., gives $[\alpha]_D - 97.8^\circ$. In all these cases, the value of $[\alpha]_D$ is increased by increasing the amount of alkali.

Béchamp (Abstr., 1891, 339) has shown that casein is slightly soluble in water, and with such a solution he found $[\alpha]_D - 105^\circ$, which is practically the same as the value found for the salts. The specific rotatory power is therefore a constant, and may be utilised in comparing milks from different sources.

E. G.

Casein and Paracasein in some of their Relations to Bases and Acids. LUCIUS L. VAN SLYKE and EDWIN B. HART (*Amer. Chem. J.*, 1905, 33, 461—496. Compare Abstr., 1903, i, 215).—The existence of two calcium compounds of casein, one of which contains about 2.40 per cent. and the other about 1.50 per cent. of calcium oxide (Söldner, Abstr., 1889, 634), has been confirmed. The former of these salts is termed basic calcium casein, and the latter normal calcium casein. Neither of these calcium compounds is coagulated by rennet enzyme alone, but the normal calcium casein is coagulated by rennet in presence of soluble calcium salts. Both compounds are coagulated if heated to 35—45° with a soluble calcium salt, such as calcium chloride. The normal calcium casein behaves in these respects just

like milk-casein, and it is probable that the casein of cow's milk exists in the form of this compound.

The base-free casein, prepared directly from milk or by treating a solution of casein in calcium hydroxide with acid until it is acid to litmus, is readily soluble in 5 per cent. sodium chloride or in hot 50 per cent. alcohol. This substance was formerly regarded as a casein mono-salt (or unsaturated salt) of the acid used in its precipitation. On treating free casein with dilute acids, salts are formed which correspond with the compounds previously termed di-salts (or saturated salts).

Paracasein closely resembles casein in its chemical properties and yields two calcium salts containing 2.40 and 1.50 per cent. of calcium oxide respectively, but whilst the normal calcium salt of casein is not coagulated by soluble calcium salts, except on warming to 35—45°, that of paracasein is readily coagulated at the ordinary temperature. It is therefore probable that paracasein only differs from casein in consisting of larger molecular aggregates. Free paracasein appears to be identical with the substance which was formerly regarded as a mono-salt of the acid used in its preparation, whilst its compounds with acids are apparently the substances previously termed di-salts. Thus the substance which is extracted from cheese by means of salt solution or hot alcohol, and was previously regarded as paracasein monolactate, has now been found to consist of free paracasein.

When an acid is formed in, or added to, milk, it unites with the calcium combined with the casein and the free casein is precipitated. On further addition of acid, the casein combines with it to form a casein salt; in the case of lactic acid, the substance so formed is the ordinary coagulum which is produced when milk turns sour. The coagulum formed by the action of rennet enzyme on milk is calcium paracasein, either mixed or loosely combined with soluble calcium salts. In the manufacture of cheddar cheese, the lactic acid produced reacts with the calcium paracasein with formation of free paracasein and calcium lactate.

The following nomenclature is suggested. The compound existing in cow's milk is called calcium casein, the term casein being reserved for the free proteid. The substance containing 2.40 per cent. of calcium oxide is termed basic calcium casein, and the compounds formed by the union of the proteid with acids are called casein salts of the acids. A similar nomenclature is applied to paracasein and its compounds; the term calcium paracasein, however, is reserved for the uncoagulated form, whilst the coagulated form is referred to as coagulated calcium paracasein.

E. G.

Presence of Fibrinoglobulin in Fibrinogen Solutions. WILLEM HUISKAMP (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 13, 610—612; *Zeit. physiol. Chem.*, 1905, 44, 182—197).—Calugareanu (*Arch. intern. Physiol.*, 2, 12) states that the addition of sodium fluoride to the extent of 3 per cent. to plasma produces fibrin formation. What really occurs, however, is a precipitate of fibrinogen; in oxalate plasma this is gelatinous, in ox or rabbit's plasma it is flocculent. It may be redissolved and made to clot, that is, it is

converted into fibrin by means of fibrin ferment. The liquid residue then contains no fibrinoglobulin. Sodium fluoride is a good precipitant for fibrinogen, and leaves the fibrinoglobulin in solution when it is present, as in plasma or fibrinogen solutions as prepared by the ordinary method. Hammarsten believes that under the influence of fibrin ferment or of heat, the fibrinogen molecule is split into fibrin and fibrinoglobulin, or else that fibrinoglobulin is a changed soluble fibrin. The latter proteid, however, is not formed in this way. It is present before clotting takes places.

W. D. H.

Spectroscopy of Oxyhæmoglobin. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, 140, 1060—1062).—Oxyhæmoglobin, when crystallised, is not to be regarded as the same thing as the pigment of the red corpuscles during life. The principal ground on which this conclusion is reached is that solution of the crystals shows a third absorption band with its centre at $\lambda = 634$. Desiccation, exposure of the crystals to the air, and numerous reagents increase the intensity of this band. By treatment with small quantities of sodium fluoride, its centre shifts to $\lambda = 612$. This may even be used for the detection of quite small amounts of fluoride.

W. D. H.

A Fluorine Combination of Methæmoglobin. J. VILLE and E. DERRIEN (*Compt. rend.*, 1905, 140, 1195—1197. Compare this vol., i, 399).—The change produced by the addition of sodium fluoride or hydrofluoric acid to methæmoglobin led to a search for a fluorine compound of this pigment. This was obtained in the form of crystals, which, however, rapidly decompose with the formation of methæmoglobin.

The spectrum of the fluorine preparation is characterised by two absorption bands, of which the centre of the first is at $\lambda = 612$, and of the second at $\lambda = 494$. The two middle bands have disappeared. The spectrum of oxyhæmoglobin is not modified by sodium fluoride. No reference is made to the work of Piettre and Vila (see preceding abstract).

W. D. H.

Identity of Phylloerythrin, Bilipurpurin, and Cholehæmatin. LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1904, 505—508).—The substance prepared from herbivorous bile by Loebisch and Fischler and named by them bilipurpurin is the same material previously named cholehæmatin by MacMunn. Gamgee suggested that cholehæmatin is identical with phylloerythrin; this, mainly on spectroscopic grounds, is shown to be correct.

W. D. H.

Organic Chemistry.

Catalytic Action of Finely Divided Metals. A. MAILHE (*Chem. Zeit.*, 1905, 29, 462).—This is a summary of the work done by Sabatier and Senderens, the author, and others on the catalytic action of finely divided iron, nickel cobalt, and copper (compare this vol., i, 401, and references therein given).

Sabatier and Senderens have quite recently converted aliphatic nitriles into amines by passing them over nickel at 180° in presence of hydrogen; benzonitrile under this treatment, however, gives toluene and ammonia, but not benzylamine. P. H.

Changes effected by Time on Hydrocarbon Substances of Organic Origin. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1905, [viii], 5, 165—174).—A *résumé* of work already published (compare Abstr., 1900, i, 3; this vol., i, 169). M. A. W.

Physical Properties of Propane. PAUL LEBEAU (*Compt. rend.*, 1905, 140, 1454—1456).—Propane, prepared from *n*-propyl iodide or from isopropyl iodide or chloride (compare this vol., i, 401), boils at -44·5° under 757 mm. pressure, has a critical temperature 97·5°, and critical pressure 45 atmos. These results are in close agreement with the values already found by Olszewski (compare *Bull. Acad. Sci. Cracow*, 1889). Both propane and ethane are liquid at -195°, and in this respect differ from methane, which solidifies at -184° (compare Olszewski, Abstr., 1885, 860, and Moissan and Chavanne, this vol., i, 253). The solubility of propane in various solvents has been determined, and the results are comprised in the following table:

	Pressure in millimetres of mercury.	Temperature.	Volumes of gas dissolved in 10 vols. of solvent.
Water	753	17·8°	0·65
Alcohol	754	16·6	790
Ether	757	16·6	926
Chloroform	„	21·6	1299
Benzene	„	21·5	1452
Turpentine	„	17·7	1587

M. A. W.

Preparation of Methyl Bromide. WILHELM STEINKOPF and WILHELM FROMMEL (*Ber.*, 1905, 38, 1865—1868).—An apparatus is figured for the preparation of methyl bromide by the action of bromine on a mixture of methyl alcohol and red phosphorus. The product is passed through water and aqueous sodium hydroxide, then over potassium hydroxide and calcium chloride, cooled in a condenser surrounded by a freezing mixture, and collected in a receiver cooled by solid

carbon dioxide. Methyl bromide is a mobile liquid at -84° , solidifies to a white, crystalline mass when cooled by liquid air, and boils at 4.5° under 758 mm. pressure. To observe the correct boiling point, it is necessary to surround the distillation apparatus completely with water at 6° , otherwise too high a boiling point is observed (compare Bunsen, *Annalen*, 1843, **46**, 44; Pierre, *Ann. Chim. Phys.*, 1845, [iii], **15**, 373; Pierre and Puchot, *Compt. rend.*, 1872, **75**, 1442). G. Y.

Action of Metal-ammonium Compounds on Halogen Derivatives of Methane. E. CHABLAY (*Compt. rend.*, 1905, **140**, 1262—1263).—When methyl chloride is passed into a solution of sodammonium, sodium chloride, methane, methylamine, and ammonia are produced according to the equation $2\text{NH}_3\text{Na} + 2\text{CH}_3\text{Cl} = 2\text{NaCl} + \text{CH}_4 + \text{NH}_2\cdot\text{CH}_3 + \text{NH}_3$.

Chloroform reacts with sodammonium, but the change is of a complex character; sodium chloride, sodamide, and sodium cyanide are formed as solid products, and methane mixed with small quantities of ethylene and acetylene is evolved.

Iodoform dissolves in liquid ammonia, and on cooling to -78° the solution deposits white crystals of the composition $\text{CHI}_3\cdot\text{NH}_3$. The vapour pressure of the crystals is equal to 760 mm. at -14° .

Sodammonium reacts readily with the ammoniacal solution of iodoform; sodium iodide and cyanide separate, and methane mixed with small quantities of ethylene, acetylene, hydrogen, and nitrogen is evolved. The reaction between sodammonium and carbon tetrachloride is similar, the products formed being sodium chloride, sodium cyanide, methane, and a little nitrogen. H. M. D.

Action of Metal-ammonium Compounds on Alcohols. General Method for the Preparation of Alkyloxides. E. CHABLAY (*Compt. rend.*, 1905, **140**, 1343—1344).—The alkali metal is dissolved with special precautions, which are described in the original, in liquid ammonia and the solution is added gradually to the required alcohol in the case of primary alcohols and *vice versa* in the case of secondary or tertiary alcohols. With primary alcohols, action progresses rapidly, and a precipitate of the alkyloxide is formed. With secondary and tertiary alcohols, the action is slow and is masked to some extent by a secondary reaction represented by the equation $2\text{NH}_3\text{Na} = 2\text{NH}_2\text{Na} + \text{H}_2$. The alkyloxides of the *sec.*- and *tert.*-alcohols are soluble in liquid ammonia and can only be isolated, combined with alcohol, by evaporation of the solvent. The sodium derivative of trimethylcarbinol crystallises in needles containing an uncertain amount of the alcohol, which can be driven off by heating the crystals, when the alcohol-free sodium derivative is left in the form of a white powder. T. A. H.

Action of Metal-ammonium Compounds on Polyatomic Alcohols. E. CHABLAY (*Compt. rend.*, 1905, **140**, 1396—1398).—The alkali metal-ammonium compounds react with the polyatomic alcohols in the cold, and monosubstituted alkali derivatives are formed with evolution of hydrogen.

Mannitol, erythritol, glycol, and glycerol were used in the experi-

ments, and the quantities of hydrogen evolved were measured. Mannitol dissolves readily in liquid ammonia, and on evaporation crystals of the composition $C_6H_{14}O_6 \cdot NH_3$ are obtained. The dissociation tension of these is 520 mm. at 0° and 760 mm. at 14° . When excess of mannitol is added to a solution of sodammonium, the blue colour of the latter quickly disappears and the monosodium compound of mannose separates out. It is readily purified by washing with liquid ammonia, which removes the excess of mannitol. Since sodammonium slowly decomposes with the formation of sodamide, which is insoluble in liquid ammonia, it is preferable to use potassammonium when a pure product is required, potassamide being readily soluble. On evaporation of a solution of erythritol in liquid ammonia, well formed crystals of the composition $C_4H_{10}O_4 \cdot 4NH_3$ remain behind. The monopotassium derivative of erythritol was isolated in the same manner as the mannitol compound.

The same method leads to the formation of alkali derivatives of menthol and borneol.

H. M. L.

The Acidity of Commercial Ethyl Alcohol and its Variations at the Ordinary Temperature. RENÉ DUCHEMIN and JACQUES DOUULEN (*Compt. rend.*, 1905, 140, 1466—1468).—Commercial ethyl alcohol commonly contains acetic acid due to the oxidising action of the air on the alcohol; the quantity of acid varies with the time of exposure to the air, and also with the nature of the vessel in which the alcohol is kept, the increase being greater in the case of green glass vessels than white glass; this is due either to the catalytic action of the former (compare Trillat, *Abstr.*, 1903, i, 222) or to the fact that the alkali it contains is not so readily available for neutralising the acid as is the case with white glass, thus, an alcohol which contained initially 0.014 gram of acetic acid per litre showed the following changes in acidity after 34 days: +0.0024 in green glass -0.0036 in white glass; +0.0036 in tinned iron; and -0.0024 in copper. After bubbling 72 litres of air through an alcohol exactly neutralised by sodium hydroxide, the acetic acid formed amounted to 0.014 gram per litre.

M. A. W.

Action of Alkalis on Aqueous Solutions of Acetol. ANDRÉ KLING (*Compt. rend.*, 1905, 140, 1256—1259).—Acetol in aqueous solution behaves as a pseudo-acid (or aci-compound, compare Hantzsch, this vol., i, 317) in that it is only gradually neutralised by an alkali and is more acid towards the pseudo-acid indicators, phenolphthalein or litmus, than towards methyl-orange, thus, 1 mol. of acetol is neutralised by 0.01 mol. KOH in the presence of methyl-orange, but requires 0.09 mol. KOH when phenolphthalein or litmus is used as indicator. Experiments on the electrical conductivity of aqueous alkaline solutions of acetol show that the resistance of the solutions increases with the time up to a certain limit, when it becomes constant, and this is characteristic of pseudo-acids.

M. A. W.

Propionylcarbinol and its Derivatives. ANDRÉ KLING (*Compt. rend.*, 1905, 140, 1345—1347. Compare this vol., i, 172, 327, and preceding abstract).—Propionylcarbinol $OH \cdot CH_2 \cdot COEt$ (ketonic

form) or $\text{O} < \begin{smallmatrix} \text{C}^{\text{Et}} \cdot \text{OH} \\ | \\ \text{CH}_2 \end{smallmatrix}$, (aci- or pseudo-acid form), boils at $79-80^\circ$ under 30 mm. or at $153-154^\circ$ under 760 mm. pressure, has a sp. gr. 1.0365 at $15^\circ/15^\circ$ and $n_D = 1.4315$ at 14.5° , whence the mol. refraction is 21.998 (the ketonic form requires 22.216 and the aci-form 21.612). It reduces Fehling's solution and may be estimated in this way, 1 gram being equivalent to 1.36 gram of copper in the form of cuprous oxide. Cupric hydroxide oxidises it to α -hydroxybutyric acid and sodium or aluminium amalgam reduces it, forming a mixture of butanone, α -butanol and butane- $\alpha\beta$ -diol; the latter boils at $192-194^\circ$.

Propionylcarbinol yields an *oxime* melting at $60-61^\circ$ and furnishes a crystalline additive *product* with sodium hydrogen sulphite. With semicarbazide, two condensation products are formed. The first, obtained when the action takes place in water, melts at 66° and may have the constitution $\text{O} > \begin{smallmatrix} \text{CH}_2 \end{smallmatrix} \text{C}^{\text{Et}} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, and the second, produced when the two substances react in alcohol, melts at $135-136^\circ$ and is probably a true semicarbazone.

Propionylcarbinyl formate, obtained by the action of potassium formate on the chloro-derivative of the keto-alcohol, boils at $176-178^\circ$, has a sp. gr. 1.094 at $17^\circ/17^\circ$ and $n_D = 1.4245$ at 17° , whence the mol. refraction is 27.070 (the ketonic form requires 27.008); the *semicarbazone* melts at 115° .

These observations indicate that propionylcarbinol, unlike acetol (mol. refraction 17.643, calculated for the ketonic form 17.614), normally exists in the two tautomeric forms and that the aci-form alone exists in aqueous solutions. The aci-form of propionylcarbinol is less active than that of acetol, since it does not react with methyl alcohol (*loc. cit.*). The esters exist only in the ketonic form. T. A. H.

Acetylmethylcarbinol (β -Hydroxy- γ -ketobutane). ANDRÉ KLING (*Compt. rend.*, 1905, 140, 1456—1458. Compare Pechmann and Dahl, *Abstr.*, 1890, 1234).—Acetylmethylcarbinol, prepared by the action of alcoholic potassium hydroxide on β -chloro- γ -ketobutane (compare Vladesco, *Abstr.*, 1892, 810), polymerises in the presence of zinc to a crystalline solid which yields pure acetylmethylcarbinol on distillation, and a dextrorotatory isomeride ($\alpha_D = 2^\circ$ for 1 dm.) is obtained by the action of the sorbose bacteria or *Mycoderma aceti* on butan- $\beta\gamma$ -diol. Acetylmethylcarbinol is a liquid with an agreeable odour, boils at $144-145^\circ$, has a sp. gr. 1.0108 at $15^\circ/15^\circ$ and $n_D = 1.4194$ at 15° ; it is oxidised to acetic acid by Fehling's solution and the reaction is quantitative; it forms a crystalline *semicarbazide* melting at $184-185^\circ$, sparingly soluble in water, a crystalline *compound* with sodium hydrogen sulphite soluble in water, and insoluble in ether, and is reduced by sodium or aluminium amalgam forming butanone, butan- β -ol and butan- $\beta\gamma$ -diol. Like acetol and propionylcarbinol (compare *Abstr.*, 1903, i, 138, 223; 1904, i, 2), acetylmethylcarbinol exists in aqueous solution in the oxidic form, $\text{O} < \begin{smallmatrix} \text{C}^{\text{Me}} \cdot \text{OH} \\ | \\ \text{CHMe} \end{smallmatrix}$, tautomeric with the ketonic form, $\text{COMe} \cdot \text{CHMe} \cdot \text{OH}$, whilst the anhydrous compound is a

mixture of the two tautomeric forms having a molecular refraction 21.826 intermediate between the values 22.216 and 21.612 calculated for the ketonic and oxidic formulæ respectively. M. A. W.

α -Alkylhydracrylic Acids. EDMOND E. BLAISE and A. LUTTRINGER (*Bull. Soc. chim.*, 1905, [iii], 33, 635—652. Compare Abstr., 1902, i, 357, 530, and this vol., i, 168).—Trioxymethylene, previously dried and finely powdered, is suspended in benzene, and to this is added one-third of the calculated quantity of ethyl α -bromobutyrate. To start the reaction, a small quantity of ethyl α -bromobutyrate is warmed in a test-tube with a zinc-copper couple, and the contents of the tube poured into the mixture. As the reaction slackens, further quantities of the bromo-ester are added. The first product of the reaction is probably the zinc compound, $\text{ZnBr}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, which in contact with water furnishes ethyl α -ethylhydracrylate and zinc hydroxide and bromide. The secondary products, dipropyl ketone and ethyl β -hydroxy- $\alpha\gamma$ -diethylglutarate, $\text{OH}\cdot\text{CH}(\text{CHEt}\cdot\text{CO}_2\text{Et})_2$, are formed during the condensation.

α -Ethylhydracrylic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$, prepared by hydrolysis of the crude ester obtained in the foregoing reaction, and purified by means of the zinc calcium salt, is a viscous liquid, which decomposes when heated even under a pressure of 0.1 mm. The ethyl ester boils at 96.5° under 13 mm. pressure and yields an acetyl derivative boiling at $95\text{--}96^\circ$ under 11 mm. pressure; when the ethyl ester is prepared by esterification of the acid, the alcoholic hydroxyl of a portion of the ethyl ester undergoes esterification by a second mol. of the acid, forming a viscous, non-volatile liquid substance, which on heating decomposes into ethyl α -ethylacrylate and α -ethylhydracrylic acid. The phenylhydrazide of the acid $\text{OH}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ is crystalline, melts at 161° , and is slightly soluble in dry ether or benzene. The phenylurethane, prepared by the action of phenylcarbimide on the acid dissolved in alcohol, is crystalline, melts at 121° , and is readily soluble in water or ether, and slightly so in light petroleum.

α -Propylhydracrylic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CHPr}\cdot\text{CO}_2\text{H}$, similarly prepared from ethyl α -bromovalerate, is a viscous liquid, slightly soluble in water; the potassium salt crystallises in brilliant lamellæ, and the ethyl ester boils at 117° under 18 mm. pressure. The phenylhydrazide of the acid, obtained by heating the phenylhydrazine salt at $110\text{--}120^\circ$ during four hours, crystallises from warm alcohol and melts at 172° . The phenylurethane crystallises from boiling alcohol on addition of sufficient water to render the liquid turbid and melts at 116° .

α -isopropylhydracrylic acid, $\text{OH}\cdot\text{CH}_2\cdot\text{CHPr}^\beta\cdot\text{CO}_2\text{H}$, obtained from ethyl α -bromoisovalerate, crystallises from dry ether and melts at 64° . The ethyl ester boils at 110° under 18 mm. pressure. The phenylhydrazide crystallises from boiling alcohol and melts at 192° , and the phenylurethane separates from benzene in crystals and melts at 133° .

α -Butylhydracrylic acid, obtained from ethyl bromohexanoate by the general reaction and purified by means of the benzylamine salt (m. p. 80°), is a viscous liquid which does not solidify at -40° ; its ethyl ester boils at $118\text{--}122^\circ$ under 10 mm. pressure.

α-Heptylhydracrylic acid, prepared from *ethyl bromopelargonate* (a colourless liquid, boiling at 149—154° under 20 mm. pressure), crystallises from a mixture of ether and light petroleum and melts at 47—48°. The *potassium* salt forms brilliant lamellæ, and the *ethyl* ester boils at 165—166° under 22 mm. pressure. The *phenylurethane* crystallises from alcohol on addition of water and melts at 105°.

Ethyl β-hydroxy-α-diethylglutarate, $\text{OH}\cdot\text{CH}[\text{CHEt}\cdot\text{CO}_2\text{Et}]_2$, formed to a small extent during the condensation of trioxymethylene with ethyl *α*-bromobutyrate in presence of zinc or by a similar condensation with ethyl formate in place of trioxymethylene, boils at 149° under 10 mm. pressure. On hydrolysis with sodium hydroxide in aqueous solution, it yields the viscous free *acid*, which on treatment with acetyl chloride furnishes the *acetyl* derivative; this crystallises from alcohol on addition of water, melts and decomposes at 144°, yields an anilide melting at 144—145°, and when heated with a strong solution of sodium hydroxide yields *β*-hydroxy-*α*-diethylglutaric acid (m. p. 87°).

T. A. H.

Desmotropic Form of Substances of the Ethyl Acetoacetate Type in the Homogeneous State and Dissolved in Neutral Media. JULIUS W. BRÜHL and HEINRICH SCHROEDER (*Ber.*, 1905, **38**, 1868—1873. Compare this vol., i, 407).—An abstract of this paper appears in *Proc.*, 1905, **21**, 164.

G. Y.

History of the Theory of the Formation and Constitution of Ethyl Sodioacetoacetate. ARTHUR MICHAEL (*Ber.*, 1905, **38**, 1922—1937).—A polemical paper in reply to Claisen (this vol., i, 258. Compare Michael, *Abstr.*, 1901, i, 123). The formation of an additive compound, $\text{ONa}\cdot\text{CMe}(\text{OEt})_2$, is considered improbable. The view that the acetoacetate formation and similar reactions are types of aldol condensations is further supported.

J. J. S.

Preparation of Ethyl Nitrosoacetoacetate. LOUIS BOUVEAULT and ANDRÉ WAHL (*Bull. Soc. chim.*, 1905, [iii], **33**, 559—561. Compare V. Meyer, *Abstr.*, 1878, 396; Cérésolle, *Abstr.*, 1882, 1052; Wleugel, *Abstr.*, 1882, 949; Jovitschitsch, *Abstr.*, 1895, i, 447; 1896, i, 81; and Bouveault and Wahl, 1903, i, 677, and 1904, i, 556).—Ethyl acetoacetate, dissolved in alcohol, is mixed with a solution of sodium ethoxide in the same solvent, and a current of methyl nitrite is passed through the mixture. On removing the excess of alcohol by distillation, the sodium derivative of ethyl nitrosoacetoacetate is obtained, which is dissolved in water and the ester liberated by an acid and extracted with ether. Ethyl nitrosoacetoacetate, when freshly distilled, is a colourless, viscous liquid, which soon solidifies to a mass of crystals. It melts at 56°, boils at 155° under 15 mm. pressure, and gives an intense indigo-blue coloration in contact with metallic iron. In using Wolff's method for preparing this ester (*Abstr.*, 1903, i, 203), the authors find it advisable to work at a temperature between -10° and 0°. No evidence of the existence of Jovitschitsch's stereoisomeric ester (*loc. cit.*) was obtained.

T. A. H.

Preparation of Ethyl Mesoxalate. RICHARD S. CURTISS (*Amer. Chem. J.*, 1905, **33**, 603—604).—Ethyl mesoxalate can be readily prepared by saturating ethyl malonate at -15° with the nitrogen oxides obtained by the action of nitric acid on arsenious oxide. Several other substances are simultaneously produced and are at present under investigation. E. G.

New Synthesis of Oxalic Acid. HENRI MOISSAN (*Compt. rend.*, 1905, **140**, 1209—1211. Compare Abstr., 1903, ii, 365).—Dry carbon dioxide begins to react with potassium hydride at 54° , potassium formate being formed as the sole product. At 80° , the action is very energetic and a mixture of potassium formate and oxalate is produced, according to the equations $\text{KH} + \text{CO}_2 = \text{KHCO}_2$; $2\text{KH} + 2\text{CO}_2 = \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2$. The quantities of formate, oxalate, and hydrogen were measured and the hydrogen found to correspond with the oxalate as required by the second equation. Sodium hydride reacts in a similar manner. H. M. D.

Unsymmetrical Compounds of the Malonic Series. FÉLIX MARGUERY (*Bull. Soc. chim.*, 1905, [iii], **33**, 541—548).—Ethyl hydrogen malonate, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, prepared by adding hydrochloric acid to a concentrated aqueous solution of the potassium salt (Massol, Abstr., 1891, 1012), is a colourless syrup, which boils at 147° under 21 mm. pressure, has a sp. gr. 1.1759 at $19^{\circ}/19^{\circ}$, n_D 1.4275 at 19° , and when heated at 150° decomposes into ethyl acetate and ethyl malonate. *Ethyl hydrogen methylmalonate* boils at 144° under 18 mm. pressure, has a sp. gr. 1.1129 at $21^{\circ}/21^{\circ}$, n_D 1.42455, is less soluble in water than the foregoing ester, and when heated under atmospheric pressure decomposes into ethyl propionate and carbon dioxide. *Ethyl hydrogen benzylmalonate* is a slightly yellow syrup, which decomposes when heated even under reduced pressure, has a sp. gr. 1.1477 at $19^{\circ}/19^{\circ}$, n_D 1.51066, and when heated at 180° furnishes carbon dioxide and ethyl β -phenylpropionate, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$. The *potassium* salts of these three esters are very hygroscopic.

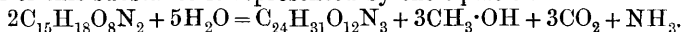
The chloride of ethyl hydrogen malonate, prepared by the action of thionyl chloride on the ester, is a mobile, colourless liquid, boils at 68 — 70° under 13 mm. pressure, and when heated under the ordinary pressure decomposes at 170 — 180° into malonic acid and ethyl malonate (compare Blaise, Abstr., 1899, i, 331). The *chloride* of ethyl hydrogen methylmalonate boils at 100° under 45 mm. pressure and the corresponding *derivative* of ethyl malonic acid at 90 — 94° under 25 mm. pressure: the *chloride* of ethyl hydrogen benzylmalonate was not obtained pure. The *amide* of ethyl hydrogen methylmalonate, prepared by the action of dry ammonia on the chloride, crystallises in needles, melts at 68 — 69° , and is very soluble in ether, benzene, or boiling carbon disulphide. The amide of ethyl hydrogen ethylmalonate is similar and melts at 90° : that of ethyl hydrogen benzylmalonate melts at 92 — 93° (compare Bischoff and Siebert, Abstr., 1887, 951). T. A. H.

Ethyl Methylethylloxalacetate and some of its Derivatives. ARTUR MEBUS (*Monatsh.*, 1905, **26**, 483—495. Compare Wislicenus and Kieswetter, Abstr., 1898, i, 240).—*Ethyl methylethylloxalacetate*,

$\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CMeEt}\cdot\text{CO}_2\text{Et}$, formed by boiling ethyl methyloxalacetate (Arnold, Abstr., 1888, 1179) with sodium ethoxide and ethyl iodide in absolute alcoholic solution in a reflux apparatus, is a yellow, mobile oil, which distils without decomposition at 134° under 14 mm. pressure, and is hydrolysed by concentrated alcoholic potassium hydroxide to oxalic and α -methylbutyric acids; by dilute sulphuric acid principally to carbon dioxide and methylethylpyruvic acid.

Methylethylpyruvic [β -methyl- α -pentanonoic] acid, $\text{CHMeEt}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, forms white crystals, melts at $30\cdot5^\circ$, boils at 90° under 12 mm. pressure, and is easily volatile in a current of steam; the *silver* and *calcium* ($+2\text{H}_2\text{O}$) salts crystallise in white leaflets. The *phenylhydrazone*, $\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$, crystallises in slender, yellow needles and melts at 130° . When reduced with sodium amalgam in aqueous solution in presence of carbon dioxide, methylethylpyruvic acid yields β -methyl- β -ethyl-lactic acid [α -hydroxy- β -methylvaleric acid], $\text{CHMeEt}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, which forms white crystals, melts on the hand, and deliquesces rapidly when exposed to the air; the *silver* and *zinc* ($+2\text{H}_2\text{O}$) salts are described. When heated with 90 per cent. sulphuric acid at 70° in a reflux apparatus, α -hydroxy- β -methylvaleric acid yields carbon monoxide and a brown oil which has no aldehyde properties. G. Y.

New Method of Preparation of Esters of Mesoxalic Acid. Condensation with Esters of Cyanoacetic Acid. CH. SCHMITT (*Compt. rend.*, 1905, **140**, 1400—1401. Compare Abstr., 1904, ii, 42; Bouveault and Wahl, Abstr., 1904, i, 556).—Esters of mesoxalic acid are obtained with a yield of 60 per cent. when the corresponding malonic esters mixed with acetic anhydride and ether are subjected to the action of a current of the nitrous gas evolved by the action of water on acid nitrosyl sulphate. Methyl and ethyl mesoxalates were thus prepared. When ethyl mesoxalate (1 mol.) condenses with ethyl cyanoacetate (1 mol.) in presence of piperidine, *ethyl cyanoethylenetricarboxylate*, $\text{C}(\text{CO}_2\text{Et})_2\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, is obtained. It can be recrystallised from ether or light petroleum and melts at $25\text{--}26^\circ$. When condensation takes place between one molecule of the mesoxalate and two molecules of the cyanoacetate, *ethyl α -dicyanopropane- $\alpha\beta\gamma$ -tetracarboxylate*, $\text{C}(\text{CO}_2\text{Et})_2[\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}]_2$, is obtained. It melts at 103° and is only slightly soluble in ether or cold alcohol. If a solution of this substance in 85 per cent. alcohol is subjected to the action of a current of hydrogen chloride, a substance of the composition $\text{C}_{24}\text{H}_{31}\text{O}_{12}\text{N}_3$, melting at 99° , is obtained on evaporation. The formation of this substance is represented by the equation



Molecular weight found 553 (theory 545).

If ethyl dicyanopropanetetracarboxylate in alcoholic solution is treated with a current of ammonia, a substance, $\text{C}_{23}\text{H}_{25}\text{O}_{11}\text{N}_3$, is obtained which melts at $105\text{--}106^\circ$. Molecular weight found 516 (theory 519). H. M. D.

[Formula for Aldehyde Hydrogen Sulphites.] ARTHUR ROSENHEIM (*Ber.*, 1905, **38**, 2005).—A correction (compare Reinking, Dehnelt, and Labhardt, this vol., i, 261, and Rosenheim and Sarow, this vol., i, 404).

W. A. D.

Condensation of Synthetical *iso*Valeraldehyde with Formaldehyde. RICHARD LICHTENSTERN (*Monatsh.*, 1905, **26**, 497—504).—The *aldol*, $\text{CPr}^{\beta}(\text{CH}_2\cdot\text{OH})_2\cdot\text{COH}$, formed by the action of 1 mol. of *iso*valeraldehyde on 2 mols. of formaldehyde in presence of potassium carbonate, is obtained as an oil which decomposes when warmed under 15 mm. pressure. The *oxime*, $\text{C}_7\text{H}_{14}\text{O}_2\cdot\text{NOH}$, forms clusters of crystals, melts at 93° , and when boiled with acetic anhydride yields the *diacetyl-nitrile*, $\text{CPr}^{\beta}(\text{CH}_2\cdot\text{OAc})\cdot\text{CN}$, which is a yellow liquid boiling at $165\text{--}168^\circ$ under 18 mm. pressure. The aldol is reduced, by aluminium amalgam in aqueous-alcoholic solution, to the *trihydric alcohol*, $\text{CPr}^{\beta}(\text{CH}_2\cdot\text{OH})_3$, which is a viscid liquid boiling at $156\text{--}158^\circ$ under 15 mm. pressure. The *triacetate*, $\text{C}_{13}\text{H}_{22}\text{O}_6$, is a colourless, viscid liquid which boils at $168\text{--}170^\circ$ under 15 mm. pressure. G. Y.

Compounds of Ketones with Ammonia. Methyl Ethyl Ketone Ammonia. CARL THOMAE (*Arch. Pharm.*, 1905, **243**, 291—294, 294—296).—When a mixture of methyl ethyl ketone with twice its volume of alcohol is saturated with ammonia at intervals during several weeks, being kept in the dark meanwhile, and the product is allowed to evaporate in the air, *methyl ethyl ketone ammonia* remains as an oil with a composition corresponding with the formula $\text{CMeEt}(\text{N}:\text{CMeEt})_2$. In one experiment, which lasted $\frac{3}{4}$ year, the yield was 77 per cent. of the theoretical. The substance appears to form salts with hydrochloric, oxalic, and picric acids, but the salts are very unstable. C. F. B.

Use of Oximino-ethers in Condensations. OTTO DIELS and GEORG PLAUT (*Ber.*, 1905, **38**, 1917—1921. Compare Abstr., 1903, i, 400).—The condensation between ethyl oxalate and β -diketones or their monoximes does not take place at all readily, but is considerably facilitated by the conversion of the monoxime into its methyl ether.

A good yield of the *methyl ether of α -isonitrosomethyl propyl ketone* $\text{COMe}\cdot\text{CEt}\cdot\text{N}\cdot\text{OMe}$, is obtained when an aqueous alkaline solution of the *isonitroso*-compound is shaken with methyl iodide for 15 hours at 100° . It is a colourless liquid distilling at $53\text{--}54^\circ$ under 32 mm. pressure, and readily condenses with ethyl oxalate in the presence of ether and sodium ethoxide (free from alcohol), yielding *ethyl δ -methyl-oximino- α -diketoheptate*, $\text{OMe}\cdot\text{N}:\text{CEt}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, which crystallises from light petroleum in stout, glistening needles melting at $40\text{--}41^\circ$ and dissolving readily in most organic solvents.

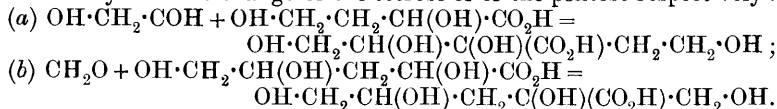
Alcoholic sodium ethoxide hydrolyses the ester, yielding *δ -methyl-oximino- α -diketoheptonic acid*, $\text{C}_8\text{H}_{11}\text{O}_5\text{N}$, the *sodium salt* of which has an intense orange-yellow colour. J. J. S.

Relationships between Carbohydrates and the Nitrogenous Products of Metabolism. FRANZ KNOOP and ADOLF WINDAUS (*Beitr. chem. Physiol. Path.*, 1905, **6**, 392—395).—5-Methyliminazole, $\begin{array}{c} \text{CMe}\cdot\text{NH} \\ | \\ \text{CH} \end{array} \text{—N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$, is formed when a solution of dextrose is exposed to sunlight at the ordinary temperature in presence of the strongly dissociated compound $\text{Zn}(\text{OH})_2\cdot 4\text{NH}_3$. It is highly probable that methyl-

glyoxal and formaldehyde are produced as intermediate products and then react with the ammonia: $C_3H_4O_2 + CH_2O + 2NH_3 = C_4H_6N_2 + 3H_2O$. The conversion of dextrose into lactic acid by means of alkali hydroxides also consists in the intermediate formation of methylglyoxal (compare also Buchner and Meisenheimer, this vol., ii, 274).

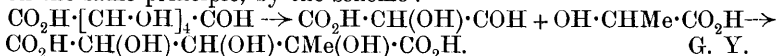
The iminazole ring formation in plants may also occur in an analogous manner, for example, pilocarpine (Pinner, Abstr., 1902, i, 232, 638), histidine (Pauly, Abstr., 1904, i, 1068). The formation of purine derivatives may be of a similar nature. J. J. S.

Formation of Saccharins from Hexoses. ADOLF WINDAUS (*Chem. Zeit.*, 1905, 29, 564. Compare Windaus and Knoop, this vol., i, 381).—Hexoses are decomposed by alkali hydroxides to two triose molecules, to a tetrose and glycolaldehyde, or to a pentose and formaldehyde, depending on the experimental conditions and the configuration of the hexose. The formation of saccharin has been explained by Kiliani as due to change of one triose molecule into lactic acid, and subsequent condensation of the unchanged aldehyde group with the α -C·OH group of the acid. The formation of parasaccharin (*a*) and of isosaccharin (*b*) may take place in the same manner, the acid being formed by isomeric change of the tetrose or of the pentose respectively:



In the formation of metasaccharin, the hexose undergoes Wolf's change without rupture of the carbon chain: $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_4 \cdot \text{COH} \rightarrow \text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$.

The formation of saccharonic acid from glycuronic acid is explained, on the same principle, by the scheme:



Circumstances which Influence the Physical Condition of Starch. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1905, 140, 1403—1406. Compare this vol., i, 312).—Starch paste prepared from potato starch is always acid to phenolphthalein and alkaline to helianthin. From the same sample of starch two pastes were prepared, distilled water being used in one case (A), ordinary supply water in the other (B). On account of the basic properties of the dissolved calcium carbonate in the supply water, the paste B was found to be less acid to phenolphthalein, and more alkaline to helianthin than the paste A. When the two pastes, each containing 4.6 per cent. of starch, were heated at 120° for half an hour and then allowed to cool, the viscosity of A was found to be much smaller than that of B. That the difference in viscosity is essentially connected with the difference in the reaction towards phenolphthalein and helianthin was shown by the fact that the viscosity of the paste A could be considerably increased by adding small quantities of calcium (sodium, potassium) carbonate to the distilled water used in its preparation.

In another experiment, the starch before being used in the prepara-

tion of the paste was treated with very dilute hydrochloric acid in order to extract the small quantity of calcium salts present, and was then carefully washed with distilled water. The paste prepared from such starch, after heating at 120° for half an hour, was found to be much less viscous than the paste A.

The observations indicate that the small quantities of salts of the alkali and alkaline earth metals which accompany starch exert a very considerable influence on the physical properties of the pastes obtained from it and are of primary importance in connection with the phenomena of liquefaction and coagulation.

H. M. D.

Constitution, Saccharification and Reversion of Starch Paste. LÉON MAQUENNE and EUGÈNE ROUX (*Compt. rend.*, 1905, 140, 1303—1308. Compare *Abstr.*, 1903, i, 679; 1904, i, 17, 227, 294; this vol., i, 262, 328, and Fernbach and Wolff, *Abstr.*, 1904, i, 374; 1905, i, 164, 312).—It is shown that natural starch grains consist of two substances, the principal one being amylocellulose, which is partially soluble in water at 100° and entirely soluble when heated with water under pressure. This substance in solution gives the characteristic blue colour with iodine, and is transformed integrally into dextrose by malt diastase, but in the solid state is unaffected by either of these reagents. Amylocellulose may exist in either the liquid (soluble) or solid (insoluble) state within a certain range of temperature and in presence of excess of water. The liquid form is produced by heating with water under pressure, and the solid form (which may be a kind of crystalline form of the substance, or a polymeric form of the liquid form) by cooling the solution so produced. The separation of the solid form under the latter condition is what has so far been known as "reversion."

The second constituent is *amylopectin*, a mucilaginous substance, which gives no colour with iodine and dissolves in extract of malt without producing a reducing sugar. The gelatinisation of starch by boiling water or alkalis is due to the presence of amylopectin, and the initial liquefaction of starch paste on the addition of malt extract is due to the action of a liquefying enzyme (*amylopectinase*) contained in the malt extract in addition to ordinary diastase (amylase). "Artificial" starch differs from the natural material only in the absence of amylopectin. The presence of amylopectin retards the separation of the solid form of amylocellulose (reversion) both in the starch grain and in starch paste.

T. A. H.

Acetyl Derivatives of Starch and Cellulose. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN TRAQUAIR (*Chem. Zeit.*, 1905, 29, 527—528. Compare *Trans.*, 1904, 85, 691).—The extent of the action of glacial acetic acid on starch at 100 — 105° is proportional to the time of heating and to the ratio between acid and carbohydrate. The acetyl compounds formed during the earlier stages of the action are insoluble in water, whilst those formed at the later stages are soluble.

The action of glacial acetic acid on cellulose is similar to that on starch.

A. McK.

Formation of Sulphuric Esters in the Nitration of Cellulose and their Influence on Stability. C. NAPIER HAKE and REGINALD J. LEWIS (*J. Soc. Chem. Ind.*, 1905, 24, 374—378).—The authors have made a number of experiments with a view to determining the causes which are responsible for the deterioration of explosives containing gun-cotton; they attribute the deterioration to the presence of sulphuric esters of cellulose derived from the latter by replacement of hydroxyl groups by the group $-\text{SO}_4\text{H}$ (compare Cross, Bevan, and Jenks, *Abstr.*, 1901, i, 672). They draw the conclusion that sulphuric acid chemically combines with cellulose during nitration to form esters which decompose into esters of a more stable character, partly by hydrolysis during washing, and partly during storage of the finished product. The difficulty of eliminating these esters explains the erratic behaviour frequently observed in explosives exposed to tropical climatic conditions. P. H.

Acetosulphates of Cellulose. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Ber.*, 1905, 38, 1859—1865. Compare *Abstr.*, 1901, i, 672).—Air-dried cotton wool (16 grams) is stirred for 20 minutes with 100 c.c. of a mixture containing equal parts of glacial acetic acid and acetic anhydride and 4.5 per cent. of sulphuric acid at 30° ; after one hour, the reaction-mixture is poured into water, when the *hydrate* of "normal" cellulose acetosulphate separates as a semi-transparent, gelatinous mass, which, after drying in air at the ordinary temperature, contains about 8 per cent. of moisture, is completely soluble in warm alcohol, and decomposes with formation of sulphuric acid on prolonged heating or warming with alcohol. "Normal" cellulose acetosulphate, $(\text{C}_6\text{H}_7\text{O}_2)_4(\text{OAc})_{10}\text{SO}_4$, obtained by drying the hydrate carefully at 90° , is hydrolysed by potassium hydroxide in 93 per cent. alcohol, forming cellulose sulphate, which is soluble in water.

If more than 5 per cent. of sulphuric acid is present in the acetic acid-anhydride mixture, a soluble *hydrate* is formed along with the hydrate of the normal ester. This has colloidal properties, can be obtained as a gelatinous precipitate by salting out, and contains a larger proportion of SO_4 than does the normal ester. If less than 4 per cent. of sulphuric acid is used, an *acetosulphate* is formed which contains less SO_4 than the normal ester, and is insoluble in alcohol but soluble in acetone. G. Y.

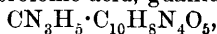
Employment of Metal-ammonium Compounds in Organic Chemistry; Formation of Primary Amines. PAUL LEBEAU (*Compt. rend.*, 1905, 140, 1264—1266. Compare this vol., i, 401).—The reaction between the metal-ammonium compounds and the halogen derivatives of the fatty hydrocarbons probably takes place in two stages. In the first stage, the metal-ammonium compound is converted into the corresponding amide and this then reacts with another molecule of the halogen compound with the formation of a primary amine. For the reaction between methyl chloride and sodammonium the equations are: $\text{CH}_3\text{Cl} + 2\text{NaNH}_3 = \text{CH}_4 + \text{NaNH}_2 + \text{NaCl} + \text{NH}_3$; $\text{CH}_3\text{Cl} + \text{NaNH}_2 = \text{CH}_3\cdot\text{NH}_2 + \text{NaCl}$. In accordance with this, it is

found that whereas sodamide has no action on the alkyl haloids at the ordinary temperature, reaction readily takes place in liquid ammonia. The quantitative investigation of the reaction between sodamide and normal propylamine shows that these react in molecular proportions in accordance with the second equation. H. M. D.

Reaction of Ammonia with Commercial Calcium Carbide.

ROBERTO SALVADORI (*Gazzetta*, 1905, **35**, i, 236—240. Compare Abstr., 1903, i, 11).—At a temperature of about 650°, calcium carbide and ammonia begin to react according to the equation $\text{CaC}_2 + 4\text{NH}_3 = \text{CaCN}_2 + \text{NH}_4\text{CN} + 4\text{H}_2$. The reaction takes place in two stages, in the first of which the calcium carbide and the nitrogen formed by the decomposition of the ammonia interact forming calcium cyanamide: $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$. The carbon thus liberated then acts on the ammonia, giving ammonium cyanide and hydrogen. The sample of carbide employed in the author's experiments contained only 78.22 per cent. of calcium carbide, the principal impurities being sulphur, silica, aluminium, iron, and magnesium, with traces of phosphorus, nitrogen, and carbon in the form of graphite; the residue insoluble in hydrochloric acid amounted to 1.73 per cent. T. H. P.

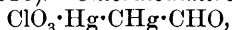
Guanidine Picrolonate. MARTIN SCHENCK (*Zeit. physiol. Chem.*, 1905, **44**, 427).—It is possible to separate guanidine from arginine and histidine by the use of picrolonic acid, guanidine picrolonate,



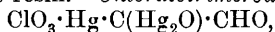
being relatively soluble in alcohol.

W. D. H.

Explosive Mercury Compounds. KARL A. HOFMANN (*Ber.*, 1905, **38**, 1999—2005. Compare Abstr., 1898, i, 635; 1899, i, 97, 485; 1900, i, 383, 384, 618).—*Chloratodimercuracetaldehyde*,



obtained by adding alcoholic acetaldehyde to a solution of mercuric oxide in aqueous chloric acid, crystallises in colourless, lustrous prisms and is exceedingly explosive, even when covered with water; on warming with sodium hydroxide and potassium cyanide, it gives the characteristic smell of aldehyde resin. *Chloratotrimercuracetaldehyde*,



obtained by passing acetylene into an aqueous solution of mercuric chlorate or of a mixture of mercuric nitrate and sodium chlorate, is slightly less explosive, and when digested with 3 per cent. hydrochloric acid gives *trichloromercuracetaldehyde*, $\text{C}_2\text{HHg}_3\text{Cl}_3\text{O}$.

Perchloratomercuracetaldehyde, obtained by passing acetylene into an aqueous solution of mercuric perchlorate, is less sensitive to shock than the corresponding chlorate.

Pyridine gives with an aqueous solution of mercuric chlorate the additive compound, $2\text{C}_5\text{H}_5\text{N} \cdot \text{Hg}(\text{ClO}_3)_2$, which crystallises in colourless needles; the *perchlorate*, $2\text{C}_5\text{H}_5\text{N} \cdot \text{Hg}(\text{ClO}_4)_2$, forms concentric aggregates of thick needles. Both these salts explode when heated, but are not sensitive to shock; they are at once decomposed by aqueous sodium hydroxide.

On passing acetylene into an aqueous solution of mercury potassium nitrite, a reddish-yellow precipitate having the composition $C_4H_6Hg_3O_6N_2$ is obtained; its nature is uncertain. Using a solution of mercuric nitrate with an excess of potassium nitrite in ice-cold water containing 1 per cent. of nitric acid, *nitritodimercuracetaldehyde*, $NO_2 \cdot Hg \cdot CHg \cdot CHO$, is obtained as a bright yellow explosive powder; that the product is a nitrite is shown by its behaviour with sulphanilic acid or α -naphthylamine in presence of acetic acid and hydrochloric acid.

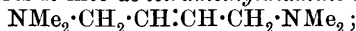
W. A. D.

Derivatives of cycloButane. RICHARD WILLSTÄTTER and WOLFGANG VON SCHMAEDEL (*Ber.*, 1905, **38**, 1992—1999).—cyclo-

Butyltrimethylammonium iodide, $CH_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} CH \cdot NMe_3I$, obtained by methylating *cyclobutylamine*, crystallises from acetone in slender, white needles and decomposes at $256-257^\circ$. When the corresponding *hydroxide*, $CH_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} CH \cdot NMe_3 \cdot OH$, is distilled, it gives a

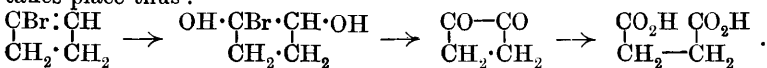
mixture of *cyclobutene*, $\begin{smallmatrix} CH_2 \cdot CH \\ | \quad | \\ CH_2 \cdot CH \end{smallmatrix}$, trimethylamine, methyl alcohol,

and *cyclobutyldimethylamine*, $CH_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} CH \cdot NMe_2$; the latter boils at $97-98^\circ$ (corr.) and gives a well-defined *aurichloride* and *picrate*. The *cyclobutene* is a gas which is absorbed by chloroform and combines additively with bromine, forming the *dibromide*, $C_4H_6Br_2$, which boils at 69.5° under 24 mm. and at $171-174^\circ$ (corr.) under the ordinary pressure, solidifies at -2° , and melts at $1-4^\circ$; the liquid has a sp. gr. 1.972 at $0^\circ/4^\circ$ and does not readily combine with aliphatic amines. Some $\alpha\delta$ -butadiene dibromide, $CH_2Br \cdot CH : CH \cdot CH_2Br$ (Thiele, *Abstr.*, 1900, i, 2), is formed together with the foregoing dibromide, and may be separated from it by the action of dimethylamine, which converts it into $\alpha\delta$ -tetramethyldiamino- Δ^2 -butene,



this boils at $39-40^\circ$ under 24—25 mm. and at $166-169^\circ$ (corr.) under the ordinary pressure.

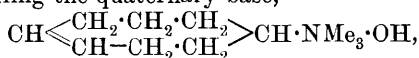
cycloButene dibromide is attacked by quinoline only at high temperatures, when red condensation products are principally formed; a little butadiene is evolved. On heating *cyclobutene dibromide* with powdered potassium hydroxide at $100-105^\circ$, Δ^1 -bromocyclobutene, $\begin{smallmatrix} CBr : CH \\ | \quad | \\ CH_2 \cdot CH_2 \end{smallmatrix}$, is obtained; it boils at $92.5-93.5^\circ$ (corr.), has a sp. gr. 1.524 at $0^\circ/4^\circ$, and on oxidation with potassium permanganate in neutral alcoholic solution, followed by oxidation of the intermediate product with chromic acid, gives succinic acid. The oxidation probably takes place thus:



When *cyclobutene dibromide* is heated with potassium hydroxide above 210° , acetylene is the principal product.

W. A. D.

*cyclo*Octenes. RICHARD WILLSTÄTTER and HANS VERAGUTH (*Ber.*, 1905, **38**, 1975—1984).—On methylating *des*-dimethylgranatanine (this vol., i, 543), decomposing the resulting methiodide with silver oxide, and distilling the quaternary base,



obtained, methylamine and water are eliminated, and a *cyclooctadiene*, C_8H_{12} , produced; it is a colourless oil, which boils at 39.5° under 16.5 mm. pressure, has a sp. gr. 0.889 at $0^\circ/4^\circ$, decolorises potassium permanganate solution, and rapidly polymerises at the ordinary temperature. *Dicyclooctadiene*, $\text{C}_{16}\text{H}_{24}$, formed in this way, crystallises from light petroleum in rosettes of thin leaflets, softens at 106° , and melts at 114° ; a second *polymeride*, $(\text{C}_8\text{H}_{12})_x$, is also formed, which is insoluble in ether, crystallises from xylene in microscopic cubes, and melts above 300° .

*cyclo*Octadiene dibromide, $\text{C}_8\text{H}_{12}\text{Br}_2$, obtained by gradually adding bromine dissolved in chloroform to *cyclooctadiene* dissolved in the same solvent, boils at $142\text{--}143^\circ$ under 14 mm. pressure; *bromocyclooctadiene*, $\text{C}_8\text{H}_{11}\text{Br}$, which is formed at the same time, boils at $93.5\text{--}94.5^\circ$ under 17 mm. pressure. Attempts to prepare a *cyclooctatriene*, C_8H_{10} , by the action of quinoline on either of the foregoing bromo-derivatives, gave always mixtures of the diene and triene. By heating the crude dibromide with dimethylamine dissolved in benzene for five hours at $130\text{--}140^\circ$, a mixture of isomeric *dimethylaminocyclooctadienes*, $\text{C}_8\text{H}_{11} \cdot \text{NMe}_2$, is obtained, distilling between 64° and 79° under 11 mm. pressure; the derived *methiodides* differ in their solubility in alcohol. The more soluble methiodide yields a quaternary base, which on distillation gives a *cyclooctatriene*, C_8H_{10} , boiling at $36\text{--}40^\circ$ under 13 mm. pressure.

It is probable that the hydrocarbons considered by Döbner (*Abstr.*, 1902, i, 598; 1903, i, 149) to be *cyclooctadiene* and its derivatives are not really of this nature.

W. A. D.

Nitration of Fluorobenzene. II. ARNOLD F. HOLLEMAN (*Rec. trav. Chim.*, 1905, **24**, 140—146).—The author has redetermined the relative proportions in which the *o*-, *m*-, and *p*-fluoronitrobenzenes are formed by the nitration of fluorobenzene under the conditions already described (*Abstr.*, 1904, i, 486). *o*-Fluoronitrobenzene (compare M. Holleman, this vol., i, 424) can be estimated by conversion into *o*-nitroaniline by heating it in a sealed tube with a solution of ammonia, in presence of alcohol and calcium chloride (to prevent erosion of the tube by the ammonium fluoride formed), the *meta*-isomeride remaining almost unaffected by this treatment. The greater part of the *p*-fluoronitrobenzene is first separated from the crude product by crystallisation and the remainder estimated by conversion into *p*-nitroanisole as already described (*loc. cit.*). The crude nitration product was found to contain 87.4 per cent. of *p*-fluoronitrobenzene, 12.4 per cent. of the ortho-isomeride, and 0.2 per cent. of the meta-compound. The inaccuracy of the results previously given is due to the assumption then made that, under the conditions employed, the

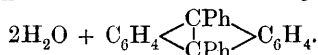
whole of the *p*-fluoronitrobenzene is converted into *p*-nitroanisole, which is now found not to be the case. T. A. H.

Two Aromatic Nitroso-compounds [*m*-Dinitrosobenzene. and *m*-Nitronitrosobenzene]. FRIEDRICH J. ALWAY and ROSS A. GORTNER (*Ber.*, 1905, 38, 1899—1901).—*m*-Dinitrosobenzene, $C_6H_4(NO)_2$, prepared by the reduction of *m*-dinitrobenzene in alcoholic solution with zinc dust and acetic acid below 0° and distilling the product with steam, forms a yellow powder melting at 146.5° to a green liquid and subsequently decomposing. The later fractions of the distillate yield crystals which are solid solutions of *m*-nitronitrosobenzene (*Abstr.*, 1903, i, 690) in *m*-dinitrobenzene. E. F. A.

Oxidation of Naphthalene to Phthalic Acid by Concentrated Sulphuric Acid in presence of Oxides or Salts of Rare Metals. HUGO DITZ (*Chem. Zeit.*, 1905, 29, 581—582).—A mixture of 25 grams of naphthalene, 375 grams of concentrated sulphuric acid, and 15 grams of the oxides formed by heating the oxalates of the rare metals obtained in the manufacture of thorium nitrate was heated in a retort. At 220° , there was a copious evolution of sulphur dioxide and carbon dioxide, and at 230° the liquid commenced to boil; at 230 — 300° , the distillate consisted of phthalic anhydride and a brown liquid, but above 300° of the anhydride only. A further quantity of phthalic anhydride was obtained by heating the liquid distillate with 5 grams of the oxide mixture. The yield of phthalic anhydride was not increased by the use of a greater proportion of the oxides, or by alteration of the order of mixing the naphthalene, sulphuric acid, and oxides.

The oxidation of naphthalene to phthalic anhydride takes place less easily, and probably with a smaller yield, in presence of the oxides of the rare metals than in presence of mercuric oxide, but the oxides of the rare metals are the more easily recovered from the reaction residue. G. Y.

Synthesis in the Anthracene Series. Condensation of Dihydroisobenzofuran Derivatives into 9:10-Substituted Anthracene Derivatives. ALFRED GUYOT and J. CATEL (*Compt. rend.*, 1905, 140, 1460—1464. Compare this vol., i, 226).—1:1:2-Triphenyl-1:2-dihydroisobenzofuran is readily converted by the action of concentrated sulphuric acid into 9:10-diphenylanthracene, the following equations representing the probable course of the reaction: $C_6H_4 \begin{smallmatrix} \text{CPh}_2 \\ \diagup \quad \diagdown \\ \text{CHPh} \end{smallmatrix} O + H_2O \rightarrow C_6H_4 \begin{smallmatrix} \text{CPh}_2 \cdot OH \\ \diagup \quad \diagdown \\ \text{CHPh} \cdot OH \end{smallmatrix} \rightarrow$



1:2-Diphenyl-1:2-dihydroisobenzofuran and its isomeride, 1:1-diphenyl-1:2-dihydroisobenzofuran, similarly yield 9-phenylanthracene; 1:1:2-triphenyl-2-dimethylaminophenyldihydroisobenzofuran and its isomeride yield 9:9:10-triphenyl-10-dimethylaminophenyl-9:10-dihydroanthracene, which yields the two stereoisomeric forms of 9:10-tetramethyldiaminodiphenyl-9:10-diphenyldihydroanthracene

(compare this vol., i, 188, 270) on heating in acetic acid solution with dimethylaniline; *o*-benzhydryltriphenylcarbinol yields 9:10-diphenylanthracene; *o*-dibenzhydrylbenzene and its isomeride, the *carbinol*, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$, yield 9-phenylanthracene.

The *carbinol*, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$, is obtained from the phthalide by the action of magnesium phenyl bromide, and yields 1:1-diphenyl-1:2-dihydroisobenzofuran, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CPh}_2 \end{smallmatrix}\rangle\text{O}$, on simple dehydration.

M. A. W.

Reduction of Nitro-derivatives with Sodium Hyposulphite.

JULES ALOY and RABAUT (*Bull. Soc. chim.*, 1905, [iii], 33, 654—655. Compare Abstr., 1904, i, 870, and this vol., i, 429).—The authors find that nitrobenzene, α -nitronaphthalene, *o*- and *p*-nitrophenols, and nitromethane can be reduced to the corresponding amines by the use of sodium hyposulphite. The latter reagent also reduces inorganic nitrites in presence of alkalis, forming ammonia, but does not attack nitrates.

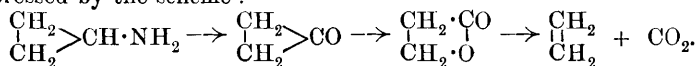
T. A. H.

Aminocyclopropane. NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 304—317. Compare Abstr., 1901, i, 509).—Aminocyclopropane, obtained previously by the author (*loc. cit.*), has been further studied. It boils at 49.5—50° under 760 mm. pressure, has the sp. gr. 0.8343 at 0°/0° and 0.8131 at 20°/0° and n_D 1.4210 at 20°. The *hydrobromide*, $\text{C}_3\text{H}_5\cdot\text{NH}_2\cdot\text{HBr}$, is readily soluble in water or alcohol, and crystallises from the latter alone or mixed with ether in needles melting at 153.5—155°. The *aurichloride*, $\text{C}_3\text{H}_8\text{NCl}\cdot\text{AuCl}_3\cdot\text{H}_2\text{O}$, crystallises in quadratic plates readily soluble in water. The corresponding *benzenesulphonamide*, $\text{C}_3\text{H}_5\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CH}\cdot\text{N}(\text{SO}_2\text{Ph})_2$, crystallises from alcohol in prismatic needles melting at 119.5—120°. *Benzoylamino*cyclopropane, $\text{C}_3\text{H}_5\cdot\text{NHBz}$, crystallises from methyl or ethyl alcohol in long needles melting at 98.5°.

Phenylcyclopropylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle$, crystallises from methyl alcohol in prismatic needles melting at 153°.

Phenylcyclopropylthiocarbamide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_3\text{H}_5$, separates from methyl alcohol in many-faced crystals melting at 123—123.5° and dissolves readily in benzene, but only slightly in light petroleum.

At the ordinary temperature, an aqueous solution of aminocyclopropane readily reduces freshly precipitated silver oxide suspended in water, and alkaline permanganate is rapidly decolorised by it. Oxidation of aminocyclopropane with chromic acid yields acetaldehyde, but if the oxidation is effected in presence of sulphuric acid, only ethylene and carbon dioxide are formed, the reaction in this case being probably expressed by the scheme:



Treatment of the amine with nitrous acid yields allyl alcohol.

T. H. P.

Hydrofluorides of some Anilides and Substituted Anilines.

RUDOLF F. WEINLAND and H. LEWKOWITZ (*Zeit. anorg. Chem.*, 1905, **45**, 39—51).—The following, mostly well-crystallised, strongly acid substances, were prepared: from acetanilide, $\text{NHPhAc}\cdot\text{HF}$; from *p*-acetotoluide, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHAc}\cdot\text{HF}$; from benzanilide, $\text{NHPhBz}\cdot\text{HF}$; from *p*-hydroxyacetanilide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot 3\text{HF}\cdot 2\text{H}_2\text{O}$; from *p*-methoxyacetanilide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot\text{HF}$; from *p*-ethoxyacetanilide, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot\text{HF}\cdot\text{H}_2\text{O}$ and also $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}\cdot 3\text{HF}\cdot 2\text{H}_2\text{O}$; from *p*-bromoacetanilide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NHAc}\cdot\text{HF}\cdot\text{H}_2\text{O}$. In air, these substances lose hydrofluoric acid, and in pure water or alcohol dissociation is complete. The following crystalline hydrofluorides of the parent amines of the above anilides were prepared: (1) from aniline, $\text{NH}_2\text{Ph}\cdot\text{HF}\cdot 1\frac{1}{2}\text{H}_2\text{O}$, $\text{NH}_2\text{Ph}\cdot 2\text{HF}$, and $\text{NH}_2\text{Ph}\cdot 3\text{HF}\cdot \frac{1}{2}\text{H}_2\text{O}$; (2) from *p*-aminophenol, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 3\text{HF}\cdot 1\frac{1}{2}\text{H}_2\text{O}$; (3) from *p*-aminophenetole, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 2\text{HF}$; (4) from *p*-aminobenzoic acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot 2\text{HF}$; (5) from *p*-bromoaniline, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2\cdot 3\text{HF}\cdot\text{H}_2\text{O}$; (6) from *o*-, *m*-, or *p*-nitroaniline, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 3\text{HF}\cdot\text{H}_2\text{O}$. D. H. J.

[Thioanilines.] OSCAR HINSBERG (*Ber.*, 1905, **38**, 1901—1902).

—The author emphasises that, as previously shown (this vol., i, 339), on fusing together aniline, aniline hydrochloride, and sulphur at 170—180° a mixture is obtained of diphenylamine, dithioaniline, melting at 76—77°, Merz's thioaniline, and a thioaniline melting at 58° (compare Hofmann, this vol., i, 427). The colourless dithioaniline described by Hofmann (*Abstr.*, 1895, i, 132), melting at 80° and forming an acetate melting at 205°, is not identical with the yellow dithioaniline, which melts at 76—77° and forms an acetate melting at 182°.

E. F. A.

Action of Aniline on Ethylcarbylamine Dibromide.

H. GUILLEMARD (*Bull. Soc. chim.*, 1905, [iii], **33**, 652—654. Compare *Abstr.*, 1904, i, 563).—When aniline, dissolved in chloroform, is added to a solution of ethylcarbylamine dibromide in the same solvent, aniline hydrobromide is precipitated, and, on evaporating the mother liquor and washing the residue with ether, *diphenylethylguanidine hydrobromide* is obtained, which crystallises in colourless needles, melts at 180—182°, and, on treatment with potassium hydroxide and subsequent extraction with ether, yields the free base, $\text{NEt}\cdot\text{C}(\text{NHPh})_2$, in the form of a viscous, faintly yellow, alkaline syrup, which boils and decomposes at 145—147° under 50 mm. pressure.

Diphenylethylguanidine reacts with carbon disulphide, forming *s*-diphenylthiocarbamide and ethylthiocarbimide, and with water only, at 250°, yielding diphenylcarbamide and ethylamine with the secondary products aniline and carbon dioxide; with solution of potassium hydroxide in water, the hydrolysis goes more easily and no secondary products are formed.

Ethylcarbylamine dibromide reacts in a similar manner with other primary and secondary amines.

T. A. H.

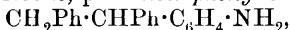
Products of the Action of Magnesium Organic Compounds on Alkylidene Bases. MAX BUSCH and ARTHUR RINCK (*Ber.*, 1905, 38, 1761—1772. Compare *Abstr.*, 1904, i, 663).—When α -anilinoethylbenzene, $\text{NHPh}\cdot\text{CHPhMe}$, is oxidised in acetone solution with potassium permanganate, a yellow oil is obtained, which is probably *acetophenoneanil*, $\text{NPh}\cdot\text{CMePh}$, as it is rapidly decomposed by dilute sulphuric acid into aniline and acetophenone. On heating α -anilinoethylbenzene hydrochloride with aniline hydrochloride at 210 — 220° , it is transformed into *p-aminodiphenylethane*, $\text{CHMePh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, a brown oil, which gives a *sulphate* crystallising in white needles and melting at 206 — 207° ; the *benzoyl* derivative, $\text{CHMePh}\cdot\text{C}_6\text{H}_4\cdot\text{NHBz}$, crystallises from alcohol in white leaflets and melts at 128° .

α -Anilinopropylbenzene, $\text{NHPh}\cdot\text{CHEtPh}$, prepared from benzyldieneaniline and magnesium ethyl iodide, forms a slightly yellow, viscid oil and boils at 192° under 20 mm. pressure; the *nitrate*, $\text{C}_{15}\text{H}_{17}\text{N}\cdot\text{HNO}_3$, crystallises in transparent needles or prisms and melts at 174° ; the *hydrochloride* forms long, white needles and melts at 187° .

α -Anilinobutylbenzene, $\text{NHPh}\cdot\text{CHPr}^a\text{Ph}$, prepared from benzyldieneaniline and magnesium propyl iodide, boils at 200° under 20 mm. pressure; the *nitrate* forms large, colourless crystals melting at 168° ; the *hydrochloride* forms slender, white, silky needles and melts at 205° .

α -Anilinoisohexylbenzene, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^b$, prepared from benzyldieneaniline and magnesium *isoamyl* iodide, boils at 212 — 215° under 20 mm. pressure and forms a viscid oil with a blue fluorescence; the *nitrate* crystallises from dilute alcohol in white needles and melts at 155° ; the *hydrochloride* melts at 206° .

α -Anilino- $\alpha\beta$ -diphenylethane, $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\text{Ph}$, from benzyldieneaniline and magnesium benzyl chloride, crystallises from alcohol in colourless, prismatic needles, melts at 56° , and boils at 247 — 248° under 18 mm. pressure; the *nitrate* forms colourless, prismatic crystals and melts at 132° ; the *hydrochloride* forms aggregates of needles, melts at 192° , and when heated with aniline hydrochloride is transformed largely into stilbene, *p-aminotriphenylethane*,



being formed only to the extent of 10 per cent. of the theoretical quantity; the *hydrochloride* of the base crystallises in colourless needles and melts at 230° .

Anilindiphenylmethane, $\text{NHPh}\cdot\text{CHPh}_2$, prepared from benzyldieneaniline and magnesium phenyl bromide, crystallises from absolute alcohol in colourless, prismatic needles, melts at 58° , and boils at 232 — 234° under 20 mm. pressure; the *nitrate* melts at 160° . When the hydrochloride of the base is heated with aniline hydrochloride for 6 hours at 210° , *p-aminotriphenylmethane* is obtained with a yield of 85 per cent. of the theoretical.

p-Toluidinodiphenylmethane, $\text{CHPh}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared from benzyldiene-*p*-toluidine and magnesium phenyl bromide, crystallises from absolute alcohol in lustrous prisms, melts at 91° , and boils at 237 — 238° under 15 mm. pressure; the *hydrochloride* forms slender, white needles and melts at 196° . *o-Toluidinodiphenylmethane*, prepared in a similar manner from benzyldiene-*o*-toluidine, crystallises from absolute alcohol in short prisms, melts at 84° , and boils at 228 — 234°

under 12 mm. pressure; the *hydrochloride* forms sheaves of thick needles, melts at 142° , and when heated with *o*-toluidine hydrochloride gives *diphenyl-p-aminotolylmethane*, $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$. This base is isolated in the form of the *sulphate*, which crystallises from alcohol or dilute sulphuric acid in slender, white needles and melts at 151° . *Tolyl**diphenyl-p-benzoylaminomethane* crystallises from alcohol in small, white, transparent prisms and melts at 187° .

o-Anisidinodiphenylmethane, $\text{CHPh}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, prepared from benzyldiene-*o*-anisidine and magnesium phenyl bromide, crystallises from alcohol in transparent prisms, melts at 92° , boils at $244\text{--}245^{\circ}$ under 15 mm. pressure, and gives a *hydrochloride* crystallising from alcohol in needles and melting at 162° . *p-Anisidinodiphenylmethane*, prepared similarly from benzyldiene-*p*-anisidine, crystallises from alcohol in sheaf-like aggregates of needles, melts at 81° , and boils at $252\text{--}255^{\circ}$ under 12 mm. pressure; the *hydrochloride* melts at 187° and the *nitrate* at 153° .

a-Anilino-a-p-isopropylphenylethane, $\text{C}_6\text{H}_4\text{Pr}^s \cdot \text{CHMe} \cdot \text{NHPh}$, prepared from cuminyldieneaniline and magnesium methyl iodide, crystallises from dilute alcohol in long, colourless needles, melts at 59° , and boils at 200° under 15 mm. pressure; the *hydrochloride* crystallises from a mixture of alcohol and ether in thick needles and melts at 177° .

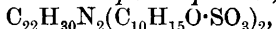
Anilinophenyl-a-naphthylmethane, $\text{NHPh} \cdot \text{CHPh} \cdot \text{C}_{10}\text{H}_7$, prepared from benzyldieneaniline and magnesium α -naphthyl bromide, crystallises from a mixture of benzene and light petroleum, melts at 112° , and boils at 270° under 15 mm. pressure; the *hydrochloride* melts at 186° .

Magnesium methyl iodide seems to combine additively with phenylbenzyldienhydrazine, but the product could not be isolated owing to its decomposing in presence of water into aniline and acetophenone.

W. A. D.

Asymmetric Nitrogen. XIX. EDGAR WEDEKIND (*Ber.*, 1905, 38, 1838—1844).—The author has prepared α -phenylbenzylmethylallyl-ammonium hydroxide from the corresponding active α -iodide, and finds that it has relatively constant rotatory power. If its aqueous-alcoholic solution is left either in the light or the dark, or if it is heated to 70° , no change occurs in the rotation. When the solution is boiled for two hours, however, the specific rotation diminishes considerably, owing to decomposition of the base. In a mixture of alcohol and water, the hydroxide has the specific rotation $[\alpha]_D + 75.5^{\circ}$ at 18° and the molecular rotation $[M]_D + 192.6^{\circ}$, which is very nearly identical with that of the corresponding active iodide, namely, $+192^{\circ}$ (see Pope and Peachey, *Trans.*, 1899, 75, 1127).

Ethylenedikairolinium di-d-camphorsulphonate,

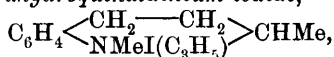


crystallises from a mixture of alcohol and ether in almost colourless needles melting at 228° , and has $[\alpha]_D + 14.84^{\circ}$. On fractional precipitation of the alcoholic solution with ether, fractions were obtained giving for $[\alpha]_D$ the values 14.84° , 12.39° , 13.42° , and 15.45° , and melting at 229° , 228° , 228° , and 224° respectively. Hence no resolution of the base takes place under these conditions; in fact, the ethylenedikairolinium dibromide prepared from the first of the above

fractions, after crystallisation from a mixture of alcohol and ether, is inactive.

Ethylenedikairolinium di-d-bromocamphorsulphonate was prepared and was separated into two fractions, of which the more sparingly soluble one was separated by crystallisation from a mixture of alcohol and ether into two fractions; the first (I) gives $[\alpha]_D + 58.1^\circ$ and $[M]_D + 547.7^\circ$, and the second (II) $[\alpha]_D + 56.08^\circ$ and $[M]_D + 528.3^\circ$. The molecular rotation of the *d*-bromocamphorsulphonic ion is $+270^\circ$, so that the active cation in fraction I has the $[M]_D + 7.7^\circ$. On precipitating the concentrated solution of fraction I with potassium bromide, the ethylenedikairolinium dibromide obtained gave $[\alpha]_D + 31.12^\circ$ and $[M]_D + 150^\circ$, values which are much greater than would be arrived at from the molecular rotation of the *d*-bromocamphorsulphonate. By means of the bromocamphorsulphonate, an active base is hence obtained which contains two asymmetric nitrogen atoms and is of the type $(OH \cdot XYZ)N \cdot CH_2 \cdot CH_2 \cdot N(ZYX \cdot OH)$; this is being further studied.

It has not yet been settled whether isomerides are obtained when inactive tertiary bases with an asymmetric carbon atom are converted into asymmetric quaternary ammonium salts. The author has prepared *methylallyltetrahydroquinaldinium iodide*,



separating from a mixture of alcohol and ether in crystals decomposing at $154-155^\circ$, by the action of excess of allyl iodide on 1-methyltetrahydroquinaldine at the ordinary temperature. When the crude product is fractionally crystallised, the last mother liquors contain a readily soluble amorphous salt, which is possibly an isomeride. T. H. P.

The Constitution of Nitrosophenols and the Conception of ortho-, meta-, and para-Positions. RAYMOND VIDAL (*Chem. Zeit.*, 1905, 29, 486).—The substance obtained by the action of nitrous acid on phenol may react either as nitrosophenol or as quinoneoxime. It is reduced in alkaline solution into *p*-aminophenol, showing that in presence of alkali the nitrosophenol form is predominant, whereas reduction in acid solutions yields, together with a small quantity of *p*-aminophenol, an amorphous, dark brown, condensation product of the unstable quinoneimide, which is primarily formed by the reduction of the quinoneoxime.

The behaviour of cresols towards nitrous acid is discussed, and a theory of the configuration of substituted benzene derivatives is put forward to account for the influence of the methyl group. P. H.

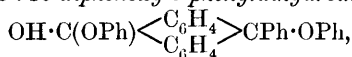
Action of Bromine on the Anthranols. CARL LIEBERMANN and LEONHARD MAMLOCK (*Ber.*, 1905, 38, 1797—1798).—On bromination with 1 mol. of bromine in carbon disulphide solution, anthranol gives rise to 10-bromoanthranol (Goldmann, *Abstr.*, 1887, 1049); when this substance is digested with methyl or propyl alcohol for 4—5 hours at 100° , *dianthranol ether*, $(OH \cdot C \left\langle \begin{array}{c} C_6H_4 \\ | \quad | \\ C_6H_4 \end{array} \right\rangle C)_2O$, is obtained in sparingly soluble crystals melting and decomposing at $235-250^\circ$.

Resorcinylanthranol, $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_3(\text{OH})_2$, prepared by heating 10-bromoanthranol with resorcinol in benzene solution, separates from alcohol saturated with sulphur dioxide on adding water saturated with the same gas in microscopic crystals, darkens at 150° , and melts and decomposes at 200° ; the *triacetyl* derivative, $\text{C}_{26}\text{H}_{20}\text{O}_6$, crystallises from alcohol and melts at $181\text{--}183^\circ$; the alcoholic solution shows a strong blue fluorescence.

10-Bromo-1:9-dihydroxyanthracene, obtained by brominating 1:9-dihydroxyanthracene, forms yellow prisms and decomposes at about 120° . W. A. D.

meso-Phenyl Derivatives of Anthracene. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1905, **38**, 1799—1805. Compare Abstr., 1904, i, 901).—2':4'-Dihydroxy-9:9-diphenyl-10-anthrone, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh} \cdot \text{C}_6\text{H}_3(\text{OH})_2$, prepared by heating phenylanthrone chloride with resorcinol and benzene, crystallises from dilute alcohol in long, colourless needles containing water of crystallisation and melts when dry at $259\text{--}261^\circ$; on acetylation, it gives the *diacetyl* derivative, $\text{C}_{30}\text{H}_{22}\text{O}_5$, which crystallises from absolute alcohol in thick, colourless plates and melts at $191\text{--}192^\circ$.

Phenylanthrone chloride combines with phenol in benzene solution, giving 10-hydroxy-9:10-diphenoxy-9-phenyldihydroanthracene,



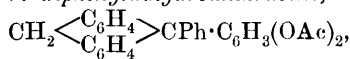
which crystallises from glacial acetic acid in white, lustrous plates and melts at $251\text{--}252^\circ$; the *acetyl* derivative, $\text{C}_{34}\text{H}_{26}\text{O}_4$, crystallises from absolute alcohol in white needles and melts at $169\text{--}171^\circ$.

10-Hydroxy-9:10-di-o-tolxyloxy-9-phenyldihydroanthracene, $\text{C}_{34}\text{H}_{28}\text{O}_3$, prepared in similar manner from *o*-cresol, crystallises from alcohol in thick, colourless plates and melts at $196\text{--}197^\circ$.

9-Ethoxy-9-phenyl-10-anthrone, $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh} \cdot \text{OEt}$, obtained by boiling phenylanthrone chloride with absolute alcohol, crystallises from the latter in rhombic plates, and melts at $156\text{--}158^\circ$.

9:9-Diphenyldihydroanthracene, $\text{CH}_2 \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh}_2$, obtained by reducing diphenylanthrone with zinc and acetic acid, crystallises from glacial acetic acid in colourless needles and melts at $195\text{--}196^\circ$.

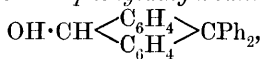
2':4'-Diacetoxy-9:9-diphenyldihydroanthracene,



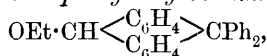
prepared in similar manner by reducing the corresponding anthrone, crystallises from absolute alcohol in small needles and melts at $212\text{--}214^\circ$.

10-Bromo-9:9-diphenyldihydroanthracene, prepared by brominating at the ordinary temperature 9:9-diphenyldihydroanthracene dissolved in carbon disulphide, crystallises from glacial acetic acid or light petroleum in colourless needles and melts and decomposes at $214\text{--}216^\circ$; when water is added to its solution in boiling glacial

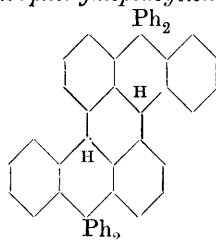
acetic acid, 10-*hydroxy*-9:9-diphenyldihydroanthracene,



crystallising from absolute alcohol and melting at 240—241°, is obtained. 10-*Ethoxy*-9:9-diphenyldihydroanthracene,



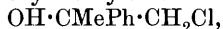
obtained by boiling the 10-bromo-compound with alcohol, preferably in presence of potassium hydroxide, crystallises from absolute alcohol in rosettes of needles and melts at 158—159°. When 10-bromo-9:9-diphenyldihydroanthracene is boiled with naphthalene, it loses its bromine and gives *tetraphenylheptacycylene*,



which forms yellowish-white crystals, does not melt at 360°, and is insoluble in all solvents. W. A. D.

Phenylmethylethylene Oxide and its Conversion into Hydratropaldehyde. AUGUST KLAGES (*Ber.*, 1905, 38, 1969—1971).

—*Phenylmethylethylene oxide*, $\text{O} \left\langle \begin{array}{c} \text{CMePh} \\ \text{CH}_2 \end{array} \right\rangle$, prepared by the action of sodium ethoxide on phenylmethylchloromethylcarbinol,



is an oil, which boils at 85—87° under 17 mm. pressure. It is readily converted into hydratropaldehyde by the action of dilute sulphuric acid. When shaken with an aqueous solution of sodium hydrogen sulphite, it forms the sodium hydrogen sulphite compound of hydratropaldehyde, from which the aldehyde was isolated and identified by its boiling point, 98—100° under 16 mm. pressure, and by the formation of its semicarbazone melting at 153°.

The *benzhydrazone*, $\text{CPh} \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \cdot \text{CHMePh}$, separates from alcohol in glistening needles and melts at 191—192°.

The *m*-nitrobenzhydrazone melts at 156—157°.

A. McK.

Methoethenylbenzene [Phenylmethylethylene] Oxide. MARC TIFFENEAU (*Compt. rend.*, 1905, 140, 1458—1460. Compare Klages, preceding abstract).—Phenylmethylethylene oxide,

$\text{O} \left\langle \begin{array}{c} \text{CPhMe} \\ \text{CH}_2 \end{array} \right\rangle$, prepared by the action of boiling aqueous potassium hydroxide or metallic sodium in ethereal solution on phenylmethylchloromethylcarbinol or by the action of powdered potassium hydroxide on an ethereal solution of the corresponding iodo-compound,

boils at 84—86° under 15 mm. pressure, has a sp. gr. 1.043 at 0°, and is converted into hydrotropaldehyde by distilling at 190—200°, or by the action of dilute acids, sodium hydrogen sulphite, or sulphurous acid (compare Abstr., 1902, i, 433, 666; also Bouveault, this vol., i, 116). Phenylmethylethylene oxide reacts with magnesium phenyl bromide to form the secondary *alcohol*, $\text{CHMePh}\cdot\text{CHPh}\cdot\text{OH}$, boiling at 185—190° under 20 mm. pressure. M. A. W.

Pinacone-pinacolin Rearrangement. P. J. MONTAGNE (*Amer. Chem. J.*, 1905, 33, 604—605).—In view of the work of Acree (this vol., i, 216), the author draws attention to his experiments (this vol., i, 58) in which he has shown that in the transformation of benzopinacone, the group in the nucleus does not change its position and that therefore the rearrangement does not take place through a ring formation. E. G.

Solubilities of Certain Organic Acids in Water at Various Temperatures. J. H. DOLIŃSKI (*Ber.*, 1905, 38, 1835—1837).—Solubility tables and curves are given for picric, sulphanilic, naphthionic, and α -naphthylamine-2-sulphonic acids in water at temperatures from 0° to 100°. The solubilities of picric and sulphanilic acids correspond very closely and are expressed by the formulæ $0.67 + 0.013t + 0.000195t^2 + 0.0000028t^3$ and $0.64 + 0.0152t + 0.00041t^2$ respectively. The solubility of naphthionic acid is very small, being given by $0.027 + 0.00024t - 0.00000255t^2 + 0.000000205t^3$, whilst α -naphthylamine-o-sulphonic acid is from 10 to 14 times as soluble. T. H. P.

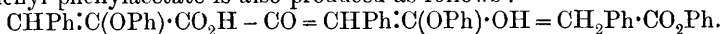
Benzhydroxamic and Dibenzhydroxamic Acids. R. MARQUIS (*Compt. rend.*, 1905, 140, 1398—1400).—If a cold solution of benzhydroxamic acid, to which potassium cyanide has been added, is left for several hours and is then acidified with acetic acid, crystals of dibenzhydroxamic acid separate. The reaction is represented by the equation $\text{OH}\cdot\text{CPh}\cdot\text{NOH} + \text{KCN} = \text{OH}\cdot\text{CPh}\cdot\text{NOBz} + \text{HCN}, \text{NH}_2\cdot\text{OH}$.

The yield of dibenzhydroxamic acid depends on the temperature, the concentration, and the quantity of the cyanide in solution, but never exceeded 50 per cent. in the author's experiments. On addition of potassium cyanide to a warm solution of benzhydroxamic acid, diphenylcarbamide and benzoic acid are formed.

Dibenzhydroxamic acid is also formed in small quantity when a solution of benzhydroxamic acid is treated with sodium nitrite, but the chief product is in this case benzoic acid. It is also obtained in 50 per cent. yield when benzhydroxamic acid is heated on the water-bath for several hours with ethyl acetoacetate. The author notes that the observed changes are rather remarkable in view of the great stability of benzhydroxamic acid towards many reagents, for example, strong sulphuric acid. H. M. D.

Elimination of Carbon Dioxide and Carbon Monoxide from α -Phenoxy-cinnamic Acids. RICHARD STOERMER and THEODOR BIESENBACH (*Ber.*, 1905, 38, 1958—1969).—When α -phenoxy-cinnamic

acid is heated at 260° , *o*-phenoxy styrene is formed, whilst carbon dioxide and carbon monoxide are evolved (compare Stoermer and Kippe, Abstr., 1904, i, 182). Owing to the elimination of carbon monoxide, phenyl phenylacetate is also produced as follows :



Phenyl phenylacetate, prepared by the Schotten-Baumann reaction from phenylacetyl chloride and phenol, crystallises in needles and melts at 42° . Since its boiling point, 158° under 7 mm. pressure, is identical with that of phenoxy styrene, it could not be separated from the latter as a product of the action of heat on *o*-phenoxy cinnamic acid, but it was identified by the formation of phenol and phenylacetic acid from it.

Phenoxy styrene boils at 157 — 158° under 7 mm. pressure. When heated under pressure with alcoholic potassium hydroxide, phenol is formed in quantitative amount, but phenylacetic acid was not detected. By the reducing action of the alcoholic potassium hydroxide, the phenylacetaldehyde formed was reduced to the corresponding alcohol, which was then transformed into styrene. The main product of the action was phenyl vinyl ether.

Phenylacetaldehyde is formed when phenoxy styrene is heated with dilute sulphuric acid.

Ethylbenzene is formed when phenoxy styrene is reduced by sodium and alcohol.

Phenoxy styrene dibromide, $\text{C}_{14}\text{H}_{12}\text{OBr}_2$, prepared by the action of bromine on phenoxy styrene, melts at 91° and gradually undergoes decomposition into the more stable *phenoxy styrene bromide*, $\text{C}_{14}\text{H}_{11}\text{OBr}$, which boils at 156° under 10 mm. pressure and separates from alcohol in needles melting at 60° .

When phenylacetaldehyde is heated under pressure with alcoholic potassium hydroxide at 190° , it forms a mixture of 1 : 3 : 5-triphenylbenzene and another hydrocarbon, probably 1 : 3-diphenyltetramethylene.

α -p-Tolyloxy cinnamic acid, $\text{CHPh}:\text{C}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})\text{CO}_2\text{H}$, prepared by the condensation of ethyl *p*-tolyloxyacetate with benzaldehyde by means of sodium (compare this vol., i, 526), melts at 166° . Oglialoro (Abstr., 1890, 320) gives 159 — 160° .

α -p-Tolyloxy- β -phenylhydracrylic acid,
 $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}_2\text{H}$,
 separates from water in silky needles and melts at 122° .

When *α -p-tolyloxy cinnamic acid* was heated at 260 — 270° , carbon dioxide and carbon monoxide were evolved, whilst the formation of an ester of phenylacetic acid was detected. *p*-Tolyloxy styrene was formed together with a crystalline isomeride which is neither an ester nor a ketone.

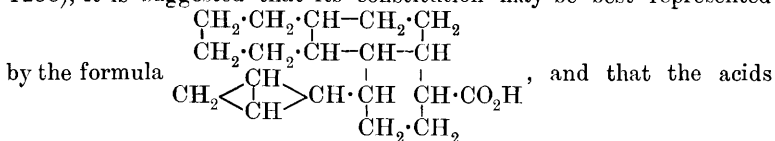
A. McK.

Constitution of Abietic Acid. HERMANN ENDEMANN (*Amer. Chem. J.*, 1905, 33, 523—534).—When abietic acid is heated with acetic anhydride at 160° in a sealed tube, an oily *monoacetyl* derivative is obtained, whence it is concluded that the acid contains one carboxyl group, but does not contain two hydroxyl groups, as stated by Tschirch and Studer (Abstr., 1904, i, 80).

By the oxidation of abietic acid with permanganic acid in acid solution, two acids, $C_{16}H_{24}O_3$ and $C_{16}H_{24}O_4$, are produced together with malonic acid, acrylic acid, and other substances, including an aromatic, neutral substance and certain syrupy acids which have not yet been identified. The acid, $C_{16}H_{24}O_4$, separates from an aqueous solution in small crystals and is soluble in chloroform or acetone, sparingly so in benzene, and insoluble in light petroleum. This acid crystallises with $1H_2O$ and melts at 80° ; after the removal of the water of crystallisation, it melts at $111-113^\circ$; it is dibasic and yields an oily *diacetyl* derivative. The *lead* and *barium* salts are described.

The acid, $C_{16}H_{24}O_3$, differs from the foregoing acid in containing an aldehyde group in place of one of the carboxyl groups. It yields the usual reactions for aldehydes, is soluble in benzene, sparingly so in water, separates from an acetone solution as a crystalline mass, and melts at 188° . The *barium* and *lead* salts were prepared.

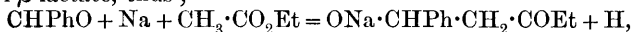
On the assumption that abietic acid is a retene derivative (compare Abstr., 1904, i, 80, and Easterfield and Bagley, Trans., 1904, 85, 1238), it is suggested that its constitution may be best represented



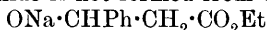
obtained by its oxidation are decahydrophenanthrenalcarboxylic acid, $C_{16}H_{24}O_3$, and decahydrophenanthrenedicarboxylic acid, $C_{16}H_{24}O_4$. It being possible that abietic acid is not so closely related to phenanthrene as is indicated by this formula and that open chains may be present, an attempt was made to ascertain if a double linking exists between two of the carbon atoms. For this purpose, a solution of the dicarboxylic acid, $C_{16}H_{24}O_4$, in chloroform was treated with excess of bromine; the results showed that whilst two atoms of bromine combined with the acid, 4 mols. of hydrogen bromide were produced, indicating that not only had substitution occurred, but that the group $-\text{CH}_2 \cdot \text{CH}_2-$ had become converted into the group $-\text{CBr} \cdot \text{CBr}-$. E. G.

β -Phenyl- β -ethylethylenelactic [**β -Hydroxy- β -phenylvaleric**] Acid. PAUL MICHNOWITSCH (*J. pr. Chem.*, 1905, [ii], 71, 427-430).— **β -Hydroxy- β -phenylvaleric acid**, $\text{OH} \cdot \text{C}(\text{Et})\text{Ph} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, formed along with the trihydric alcohol by the action of potassium permanganate on phenylethylallylcarbinol (Bogorodsky and Ijubarsky, Abstr., 1898, i, 303), crystallises in glistening leaflets, melts at $118-121^\circ$, and is easily soluble in alcohol or ether. The *barium*, *calcium*, and *silver* salts are described. G. Y.

Condensation of Benzaldehyde and Ethyl Phenoxyacetate. Claisen's Cinnamic Acid Synthesis by means of Sodium. RICHARD STOERMER and OTTO KIPPE (*Ber.*, 1905, 38, 1953-1958).—Claisen assumes that his cinnamic acid synthesis from benzaldehyde and ethyl acetate proceeds with the intermediate formation of ethyl phenyl- β -lactate, thus;



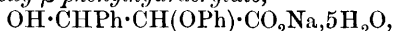
a view which is combated by Michael. The experience of the authors on the condensation of benzaldehyde with ethyl phenoxyacetate accords with Claisen's interpretation, since they have isolated α -phenoxy- β -phenylhydracrylic acid as the intermediate product. According to Claisen, sodium hydroxide is not formed from the compound



during the condensation, since he detected no products of the hydrolysis of ethyl cinnamate. The authors find, however, that when the product resulting from the condensation of benzaldehyde and ethyl phenoxyacetate by means of sodium is decomposed by the calculated amount of glacial acetic acid and water then added, the sparingly soluble sodium α -phenoxy- β -phenylhydracrylate separates, whilst only a small amount of the corresponding ester remains in the ether present together with the ethyl α -phenoxy-cinnamate, which has not undergone hydrolysis.

Aniline α -phenoxy-cinnamate, $\text{C}_{21}\text{H}_{19}\text{O}_3\text{N}$, prepared by the addition of aniline to an ethereal solution of α -phenoxy-cinnamic acid, crystallises in needles and melts at $135-136^\circ$.

Sodium α -phenoxy- β -phenylhydracrylate,



is sparingly soluble in cold water and decomposes at about 340° into benzaldehyde and phenoxyacetic acid. The *acid* is precipitated by the addition of mineral acid to the sodium salt as an oil, which, when crystallised from a mixture of benzene and light petroleum, melts at $93-94^\circ$. The *acetyl* derivative, formed by heating the acid with acetyl chloride, separates from dilute alcohol in glistening needles and melts at 149° ; when acetic anhydride is used, phenoxy-cinnamic acid is formed. The *aniline* salt separates from benzene in silvery leaflets and melts at 162° .

A. McK.

Products of the Condensation of *o*-Aldehydocarboxylic Acids. GUIDO GOLDSCHMIEDT (*Arch. Pharm.*, 1905, **243**, 296—299).—The conclusions of Gadamer (this vol., i, 368; Bruns, *ibid.*, 353) have been anticipated to a large extent by the author and his students (compare especially Fulda, *Abstr.*, 1900, i, 36). C. F. B.

Synthesis of Aromatic β -Ketonic Esters. FÉLIX MARGUERY (*Bull. Soc. chim.*, 1905, [iii], **33**, 548—551).—These esters have been prepared by the application of Friedel and Craft's reaction to the chlorides of the monoethyl esters of the malonic acid series (this vol., i, 507) and aromatic hydrocarbons (compare Bouveault, *Abstr.*, 1896, i, 551, 616, and 1897, i, 530).

Ethyl p-toluoylacetate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, is a colourless, pleasant-smelling, slightly oily liquid boiling at 170° under 30 mm. pressure; it is soluble in alcohol or benzene and insoluble in water, and gives an intensely violet coloration with alcoholic ferric chloride. The *copper* derivative forms green crystals and is soluble in chloroform. With hydrazine, the ester furnishes 3-tolylpyrazolone melting at 123° .

p-Toluoylacetic acid, obtained by hydrolysing the ester by Cérésolle's method, forms micaceous scales and melts and decomposes at 96° ,

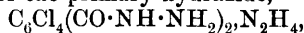
yielding carbon dioxide and a ketone which distils at 220° , and on oxidation furnishes terephthalic acid.

Ethyl 1:4-dimethylbenzoylacetate, $C_6H_3Me_2 \cdot CO \cdot CH_2 \cdot CO_2Et$, is an oily, slightly rose-coloured liquid, which boils at $176-180^{\circ}$ under 14 mm. pressure and gives an intense red coloration with ferric chloride and yields a crystalline *copper* derivative.

Ethyl 1:4-dimethylbenzoylpropionate resembles the foregoing ester, boils at $190-195^{\circ}$ under 18 mm. pressure, has a sp. gr. 1.038 at $19^{\circ}/19^{\circ}$, n_D 1.50623 at 19° , and gives a bluish-violet coloration with ferric chloride. When hydrolysed by boiling with aqueous potassium hydroxide, it yields *p*-xylyl ethyl ketone boiling at $238-240^{\circ}$.

T. A. H.

Hydrazine Derivatives of Tetrachlorophthalic Acid. ISAAC K. PHELPS (*Amer. Chem. J.*, 1905, 33, 586-590).—When ethyl tetrachlorophthalate (1 mol.) is heated with hydrazine hydrate (1 mol.) in presence of ether for 10 hours at 100° in a sealed tube, the *hydrazine* compound of the primary hydrazide,



separates; it forms yellow crystals, is insoluble in ether, and sparingly so in hot alcohol, and when heated does not melt, but becomes charred at $290-300^{\circ}$. If this compound is boiled with a hot alcoholic solution of hydrogen chloride, the *primary hydrazide*, $C_6Cl_4(CO \cdot NH \cdot NH_2)_2$, is obtained as a colourless substance which is insoluble in the ordinary organic solvents.

The *secondary hydrazide*, $C_6Cl_4 \begin{smallmatrix} < CO \cdot NH \\ & | \\ & CO \cdot NH \end{smallmatrix}$, obtained by heating tetrachlorophthalic acid (1 mol.) with hydrazine hydrate (1.5 mols.) at $140-150^{\circ}$ for half an hour under a reflux condenser, separates from glacial acetic acid in pale yellow crystals, melts and decomposes slightly at $286-287^{\circ}$, is insoluble in most organic solvents, and is soluble in aqueous alkali hydroxides and reprecipitated by acids; its *diacetyl* derivative melts at $203-204^{\circ}$; its *mono-sodium*, *mono-potassium*, and *mono-silver* salts were prepared and analysed. By the action of ethyl chlorocarbonate on the silver salt, the compound $C_6Cl_4 \begin{smallmatrix} < CO \cdot NH \\ & | \\ & CO \cdot N \cdot CO_2Et \end{smallmatrix}$ is obtained, which forms white, prismatic crystals and melts at $244-245^{\circ}$.

No evidence was obtained in these experiments of any reaction between the hydrazine and the chlorine in the benzene nucleus.

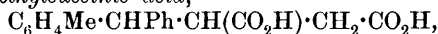
E. G.

Synthesis of Aromatic Substituted Homosuccinic Acids by means of Paraconic Acids. JOHAN F. EIJKMAN (*Chem. Centr.*, 1905, i, 1388; from *Chem. Weekblad*, 2, 229-231).—Aromatic hydrocarbons may be condensed with lactone-carboxylic acids by allowing the mixture to remain in presence of aluminium chloride for several days.

Diphenylmethylsuccinic acid, $CHPh_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, prepared from phenylparaconic acid and benzene, crystallises in needles, is

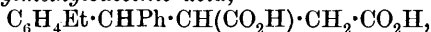
readily soluble in alcohol, less so in hot water or benzene, and sparingly so in cold water; it melts at 175° , giving off vapour and probably forming an anhydride.

Phenyltolylmethylsuccinic acid,



obtained from phenylparaconic acid and toluene, crystallises from dilute alcohol in needles and melts at 150 – 153° , forming an anhydride.

Phenylethylphenylmethylsuccinic acid,



prepared from phenylparaconic acid and ethylbenzene, crystallises from benzene or dilute alcohol in needles and melts and gives off gas at 135 – 140° .

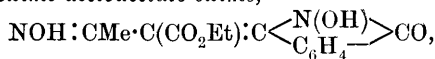
E. W. W.

isoArtemisin (δ -Hydroxysantonin). EDGAR WEDEKIND and A. KOCH (*Ber.*, 1905, **38**, 1845–1851. Compare Jaffé, *Abstr.*, 1897, i, 628; Bertolo, *Abstr.*, 1901, i, 718; Freund and Mai, *Abstr.*, 1902, i, 101; Horst, *Abstr.*, 1902, i, 387).—Chlorosantonin, $\text{C}_{15}\text{H}_{17}\text{O}_3\text{Cl}\cdot\text{H}_2\text{O}$ (this vol., i, 212), has $[\alpha]_{\text{D}} -54\cdot75^{\circ}$, is only slightly soluble in water, light petroleum, or ether, but easily so in other organic solvents, and dissolves slowly in warm aqueous sodium hydroxide. It dissolves in cold concentrated sulphuric or nitric acids, and is decomposed when warmed with the former. δ -Hydroxysantonin, $\text{C}_{15}\text{H}_{18}\text{O}_4$, is formed when chlorosantonin is heated with 1 mol. of potassium hydroxide in alcoholic solution at 100° or with excess of aqueous sodium acetate in a sealed tube at 110 – 115° . It crystallises in colourless needles, melts at 214 – 215° , has $[\alpha]_{\text{D}} -108\cdot62^{\circ}$, and dissolves readily in hot alcohol, acetone, or chloroform. It is insoluble in boiling aqueous sodium hydroxide, but dissolves in cold concentrated sulphuric or nitric acids and in hot hydrochloric acid to a yellow solution, which, on dilution, deposits a yellow product melting at 150 – 155° . The phenylhydrazone, $\text{C}_{15}\text{H}_{18}\text{O}_3\cdot\text{N}\cdot\text{NHPh}$, crystallises in yellow, microscopic needles, melts and decomposes at 176 – 178° , and dissolves in concentrated sulphuric acid to a green solution, and in fuming hydrochloric acid to a yellow solution which becomes greenish-yellow and deposits a precipitate.

G. Y.

Ethyl Phthalylacetoacetate. CARL BÜLOW [and, in part, E. SIEBERT] (*Ber.*, 1905, **38**, 1906–1917. Compare E. Fischer and Koch, *Abstr.*, 1883, 806; Bülow, *ibid.*, 1887, 144).—The phenylhydrazone of ethyl phthalylacetoacetate is not decomposed when heated with concentrated sulphuric acid at 175° or when boiled with acetic acid or anhydride. Aqueous baryta or 30 per cent. potassium hydroxide solution hydrolyses the ester to the corresponding acid, $\text{C}_{18}\text{H}_{14}\text{O}_4\text{N}_2$; this crystallises from hot water in small, compact prisms, melts and decomposes at 233 – 234° , and is readily soluble in alcohol, acetone, or acetic acid. A solution of the ammonium salt yields precipitates with solutions of the salts of most heavy metals. The hydrazone of ethyl phthalylacetoacetate, $\text{C}_{14}\text{H}_{14}\text{O}_4\text{N}_2$, obtained by the action of hydrazine hydrate on an acetic acid solution of ethyl phthalylacetoacetate, crystallises from acetic acid in small, colourless needles, melts at 290° , and is readily soluble in most organic solvents.

Ethyl phthaloxime-acetoacetate oxime,



obtained by the action of hydroxylamine hydrochloride on an acetic acid solution of the ester at the ordinary temperature, melts at 224° and is soluble in cold alkalis but insoluble in water.

3-Methyl-4-phthalyl-5-isooxazolone, $\text{CO} < \begin{array}{c} \text{O} \\ \text{C}_6\text{H}_4 \end{array} > \text{C} : \text{C} < \begin{array}{c} \text{CMe} : \text{N} \\ \text{CO} - \text{O} \end{array}$, ob-

tained by the action of hydroxylamine hydrochloride on the ester according to Schiff's method, crystallises from acetic acid in colourless needles melting at 203° , and is insoluble in alkalis, but dissolves readily in most organic solvents.

Semicarbazide and ethyl phthalylacetoacetate in alcoholic solution yield the sparingly soluble semicarbazone of *ethyl phthalylsemicarbazone-acetoacetate semicarbazone*, $\text{C}_{36}\text{H}_{18}\text{O}_5\text{N}_6(?)$, which decomposes and melts at 243° and then solidifies and melts again above 280° . The filtrate from the disemicarbazone yields *ethyl phthalylacetoacetate semicarbazone*, $\text{C}_{15}\text{H}_{15}\text{O}_5\text{N}_3$, in the form of long needles melting at $188-189^\circ$, and readily soluble in alcohol, acetone, or chloroform.

Hydrazine hydrate reacts with ethyl *o*-carboxybenzylacetoacetate (Abstr., 1887, 144), yielding *4-o-carboxybenzyl-3-methyl-5-pyrazolone*, $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_2$, which crystallises in colourless needles melting at 254° . It is both basic and acidic in character. Hydroxylamine transforms the same ester into *4-o-carboxybenzyl-3-methyl-5-isooxazolone*, $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$, which crystallises in needles, dissolves in alcohol, acetone, acetic acid, or alkalis, and melts at 173° .

Semicarbazide and the ester yield *4-o-carboxybenzyl-3-methyl-5-pyrazolone-1-carboxylamide*, $\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}_3$, which melts and decomposes at 181° and then solidifies and melts again above 200° . The readiness with which the ester of *o*-carboxybenzylacetoacetic acid forms ring compounds with hydrazine, hydroxylamine, &c., is attributed to the labile H atom, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, which is not present in ethyl phthalylacetoacetate.

J. J. S.

Indophenol Derivatives from *p*-Chlorophenol. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158091).—When *p*-chlorophenol is mixed with a molecular quantity of an alkylated *p*-diamine or *p*-aminophenol and oxidised, compounds are obtained having the composition of *o*-indophenols, $\text{O} : \text{C}_6\text{H}_3\text{Cl} : \text{N} \cdot \text{C}_6\text{H}_4\text{X}$, where $\text{X} = \text{OH}$ or NAlk_2 . Thus alkaline potassium ferricyanide oxidises a mixture of *p*-chlorophenol and dimethyl-*p*-phenylenediamine to an *indophenol* which dissolves in alcohol to a blue solution, becoming red on addition of acids. Sodium sulphide reduces it to the *leuco*-compound which forms colourless crystals becoming blue in air. A blue dye is obtained on fusing the indophenol or its leuco-compound with sodium sulphide and sulphur.

The *indophenol* from *p*-chlorophenol and *p*-aminophenol forms a green, crystalline sodium salt, dissolving in water, alcohol, or concentrated sulphuric acid to blue solutions. Similar compounds are obtained from *p*-chlorophenol and *p*-amino-*o*-cresol or 2 : 6-dichloro-4-amino-

phenol. It is not possible to replace the *p*-chlorophenol in this reaction by *p*-cresol or phenol-*p*-sulphonic acid. C. H. D.

Iodo-hydrido-compounds of Non-nitrogenous Derivatives of Anthraquinone. CARL LIEBERMANN and LEONHARD MAMLOCK (*Ber.*, 1905, 38, 1784—1796. Compare *Abstr.*, 1904, i, 901).—On passing hydrogen iodide into a cold saturated solution of anthraquinone in benzene, small, dark, lustrous leaflets of a *compound*, $2C_{14}H_{10}O, 2HI, I_2$, derived from anthranol, separate; the compound probably has the constitution $2C_6H_4 \begin{smallmatrix} \text{CHI} \\ \text{CI(OH)} \end{smallmatrix} C_6H_4, I_2$, and the mechanism of its formation is discussed in detail. On mixing molecular proportions of carbon disulphide solutions of anthranol and iodine, a *compound*, $C_{14}H_{10}O, HI, I_2$, crystallising in dark needles, is formed. In benzene solution, anthranol and hydrogen iodide give a *substance* of approximately the composition $4C_{14}H_{10}O_4, HI, I_2$. On further addition of hydrogen iodide, green crystals of $4C_{14}H_{10}O, 4HI, I_2$ are obtained. In all cases, the compounds formed give varying analytical data, owing to the readiness with which they lose a portion of their iodine.

On passing hydrogen iodide into a solution of 2-methylantraquinone in benzene, the crystalline *compound*, $C_{15}H_{12}O, HI, I_2$, derived from β -methylantranol, is obtained; on decomposition with alcohol, it gives 2-methylantranol, which melts at 80—84° and not at 100°, as stated by Limpricht (*Abstr.*, 1901, i, 145). 2-Methylantranol combines with iodine and hydrogen iodide in benzene solution to form a *compound*, $2C_{15}H_{12}O, 2HI, I_3$; with iodine alone in benzene solution, the product has the composition $2C_{15}H_{11}O, 2HI, I_2$.

With hydrogen iodide in benzene solution, phenylantranol gives a *compound*, $2C_{20}H_{14}O, 2HI, I_3$, identical with the substance obtained by a similar method from phenyloxantranol (Liebermann, Glawe and Lindenbaum, *loc. cit.*). 1-Hydroxyanthraquinone, under similar conditions, gives the *compound* $C_{14}H_{10}O_2, HI, I_3$, which is decomposed by alcohol and sulphur dioxide giving 1-hydroxy-9-antranol; this substance is better prepared by reducing 1-hydroxyanthraquinone with tin and hydrochloric acid in presence of acetic acid, and crystallises from glacial acetic acid in bright yellow needles melting at 136—138°.

The constitution of these iodo-derivatives is dealt with in detail.

W. A. D.

Anthragallolamide [2-Amino-1 : 3-dihydroxyanthraquinone]. FRIEDRICH BÖCK (*Monatsh.*, 1905, 26, 571—593. Compare Georgievics, *Abstr.*, 1886, 69).—Anthragallolamide is formed by the action of ammonium chloride on anthragallol in dilute alkali hydroxide solution, or in large quantities by exposing finely powdered anthragallol, dried at 150°, to the action of ammonia vapour for several days and heating the ammonium salt so formed at 130°; the *barium* salt, $C_{14}H_7O_4NBa$, was analysed. The *diazo-anhydride*, $C_8H_4O_2 \begin{smallmatrix} \text{C(OH):C}\cdot\text{N}_2 \\ \text{CH}=\text{C}\cdot\text{O} \end{smallmatrix}$, is formed

by the action of amyl nitrite on the amine in slightly acid alcoholic solution; it crystallises in glistening, yellow, microscopic plates, detonates when rapidly heated, is slightly soluble in water, but easily

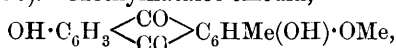
so in aqueous alkali hydroxides to red solutions, and when reduced by stannous chloride in alkaline solution yields purpuroxanthin, which melts at 270° (m. p. 263° , Plath, *Ber.*, 1877, 10, 615). This, when heated with methyl iodide and aqueous potassium hydroxide at 120° , forms the dimethyl ether which melts at 187° (m. p. 180° , Plath, *loc. cit.*) and dissolves in hot aqueous alkali hydroxide to a red solution, which deposits a red, flocculent precipitate on cooling. In one experiment, persistent methylation led to the formation of a *product*, $C_{14}H_5O_2Me(OMe)_2$, which melted at 153° and was not acted on by hot aqueous alkali hydroxides. When boiled with benzaldehyde, anthragallolamide forms a *benzylidene* derivative, $C_{14}H_7O_4N:CHPh$, which crystallises in glistening, brown prisms, melts at $257-258^{\circ}$, and is easily hydrolysed by dilute alkali hydroxides or acids or by warm pyridine; when shaken with acetic anhydride and pyridine, it forms an *acetyl* derivative as a yellow, crystalline mass, which melts at 158° and is hydrolysed by boiling alcohol. When heated with aqueous or alcoholic ammonia under pressure at 100° , anthragallol dimethyl ether (m. p. 160° , Abstr., 1903, i, 266) forms an *amino-product* which crystallises in slender, violet needles and melts at 231° . It forms a *hydrochloride* which crystallises in red needles, and when warmed yields ammonium chloride and anthragallol dimethyl ether, which is formed also by warming the amino-compound with aqueous potassium hydroxide.

G. Y.

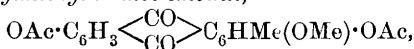
1 : 2 : 5-Trihydroxyanthraquinone. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 156960).—When alizarin is dissolved in fuming sulphuric acid (30 per cent. SO_3) to which boric acid has been added, and agitated at $30-35^{\circ}$ until a violet solution is obtained, a sulphuric ester of 1 : 2 : 5-trihydroxyanthraquinone is formed. The product is decomposed by water, and after purification and crystallisation from acetic acid yields red needles of 1 : 2 : 5-trihydroxyanthraquinone melting at $273-274^{\circ}$. The *triacetyl* derivative melts at $227-228^{\circ}$.

C. H. D.

Methylnataloe-emodin and Nataloe-emodin. EUGÈNE LÉGER (*Compt. rend.*, 1905, 140, 1464—1466. Compare Abstr., 1902, i, 549, 685; 1903, i, 356).—Methylnataloe-emodin,

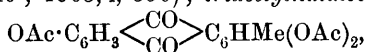


yields 4-hydroxyisophthalic acid melting at 293° (corr.) on fusion with potassium hydroxide, is oxidised to oxalic acid by fuming nitric acid, and on treatment with bromine yields a *pentabromide*, $C_{16}H_7O_5Br_5$, which crystallises in dark red needles, melts at $293-295^{\circ}$ (corr.), and is soluble in acetic acid or toluene and sparingly so in methyl alcohol. *Diacetylmethylnataloe-emodin*,



forms long, brilliant, needle-shaped crystals, melts at 169° (corr.), and is soluble in alcohol or chloroform, sparingly so in ether, and insoluble in water. Nataloe-emodin (trihydroxymethylantraquinone), obtained from methylnataloe-emodin by the action of concentrated hydrochloric

acid, melts at 214.5° (corr.) and not at 220.5° as previously stated (Abstr., 1902, i, 549; 1903, i, 356); *triacetylnataloe-emodin*,

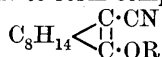


crystallises from methyl alcohol in long, bright yellow needles melting at 203.7° (corr.). M. A. W.

Menthones and Menthols obtained by the Catalytic Reduction of Pulegone with Metallic Nickel. ALBIN HALLER and CAMILLE MARTINE (*Compt. rend.*, 1905, 140, 1298—1303. Compare this vol., i, 220).—By the action of nickel sponge on pulegone at 140 — 160° , the authors have obtained a liquid which boils at 94 — 95° under 16 mm. pressure, is dextrorotatory, has $[\alpha]_D + 5^{\circ}$ to $+ 8^{\circ}$, furnishes an oily *oxime* and condenses with benzaldehyde, in presence of hydrogen chloride, forming hydrochlorobenzylidenementhone, identical with that obtained from natural menthone. This liquid is regarded as a mixture of ketones provisionally designated *pulegomenthones*. By the prolonged action of nickel sponge on pulegone at 150 — 160° , a mixture of “*pulegomenthols*” was obtained. The crude product boils at 107 — 108° under 16 mm. pressure, has the odour of menthol, and is slightly dextrorotatory ($[\alpha]_D + 6^{\circ}$ to $+ 8^{\circ}$). When cooled, the mixture partially solidifies, and by fractional crystallisation of the deposited matter from light petroleum, menthol and *α-pulegomenthol* were obtained. *α-Pulegomenthol* melts at 84 — 85° , has $[\alpha]_D + 30^{\circ}$ and $+ 23.10'$ in 4 and 10 per cent. solutions in alcohol respectively; it may be identical with Beckmann's *isomenthol* (Abstr., 1897, i, 248).

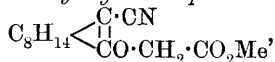
On treatment with phthalic anhydride, the oily product remaining after freezing out menthol and *α-pulegomenthol* gave a mixture of the following esters: menthyl phthalate, *α-pulegomenthyl hydrogen phthalate* (m. p. 104 — 105° and $[\alpha]_D + 27.5^{\circ}$ in 4.724 per cent. solution in alcohol), and *β-pulegomenthyl hydrogen phthalate*, which melts at 137 — 138° and has $[\alpha]_D + 8.9^{\circ}$. *β-Pulegomenthol*, regenerated from the acid phthalate, is a syrupy liquid, which does not crystallise when cooled with ice and salt, boils at 212 — 212.5° (corr.), and has $[\alpha]_D + 2.6^{\circ}$ at 14° . Carvone, on reduction with nickel sponge, furnishes a mixture of dihydrocarvols, boiling at 216 — 218° and yielding a *phenylurethane* which melts at 107 — 108° . Under the same conditions, thujone yields thujol, citronellol gives dihydrocitronellol, and terpineol furnishes hexahydrocymene. T. A. H.

Cyanocamphoracetic, α-Cyanocamphorpropionic, and α-Cyanocamphorisobutyric Acids and their Principal Derivatives. ALBIN HALLER and A. COURÉMÉROS (*Compt. rend.*, 1905, 140, 1430—1435).—Sodiocyanocamphor reacts with the halogen-substituted derivatives of the fatty acids to form compounds of the type



(compare Abstr., 1891, 1499; 1892, 1344; 1894, i, 338), and in the case of *α*-bromopropionic acid, which contains an asymmetric carbon atom, sodiocyanocamphor resolves it into its two optical isomerides,

forming a dextro- and a lævo-derivative. *Ethyl cyanocamphoracetate*, $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot O \cdot CH_2 \cdot CO_2Et \end{smallmatrix}$, prepared from sodiocyanocamphor and ethyl chloroacetate or iodoacetate in xylene solution, is an oily liquid boiling at 190—200° under 15 mm. pressure, has a sp. gr. 1.09 at 0° and $[a]_D + 79.44^\circ$, is insoluble in water or alkaline solutions, soluble in alcohol, chloroform, or benzene, and hydrolysed by hydrochloric acid, yielding cyanocamphor. *Methyl cyanocamphoracetate*,



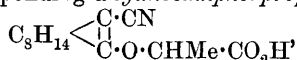
boils at 150—156° under 25 mm. pressure, melts at 67°, and has

$[a]_D + 78.10^\circ$. *Cyanocamphoracetic acid*, $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot O \cdot CH_2 \cdot CO_2H \end{smallmatrix}$, obtained by the action of alcoholic potassium hydroxide on either of the preceding compounds, crystallises from alcohol, xylene, or benzene and chloroform, melts at 98—99°, has $[a]_D + 113.69^\circ$, is insoluble in water, but soluble in ether or light petroleum. The *potassium* salt, $C_{13}H_{16}O_3NK$, forms thin, white needles soluble in water or alcohol; the *copper* salt, $(C_{13}H_{16}O_3N)_2Cu$, is a grey, amorphous powder insoluble in water but soluble in methyl or ethyl alcohol. *Cyanocamphoracet-*

amide, $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot O \cdot CH_2 \cdot CO \cdot NH_2 \end{smallmatrix}$, prepared by the action of alcoholic ammonia in sealed tubes at 100° on ethyl cyanocamphoracetate, crystallises from benzene, melts at 120°, and has $[a]_D + 95.73^\circ$. Ethyl α -bromopropionate reacts with sodiocyanocamphor to form two *ethyl-*

α -cyanocamphorpropionates, $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot O \cdot CHMe \cdot CO_2Et \end{smallmatrix}$, which are enantiomorphously related to one another; the more soluble one melts at 49°, has $[a]_D + 144.08^\circ$, and crystallises from methyl alcohol in beautiful needles; the *lævo*-compound melts at 74.5°, has $[a]_D - 33.78^\circ$, and crystallises in white plates soluble in alcohol, chloroform, or

benzene. *Methyl- α -cyanocamphorpropionate*, $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot O \cdot CHMe \cdot CO_2Me \end{smallmatrix}$, has also been obtained in two forms; the one compound melts at 44° and has $[a]_D + 175.44^\circ$ and the isomeride crystallises in the monoclinic system (Wyrouboff), melts at 80—81°, and has $[a]_D - 41.76^\circ$. By the action of alcoholic potassium hydroxide on the *dextro*-ethyl α -cyanocamphorpropionate, the corresponding *α -cyanocamphorpropionic acid*,



is obtained, which melts at 109°, has $[a]_D + 93.06^\circ$, forms *ammonium*,

silver, and *copper* salts; the *amide*, $C_8H_{14} \begin{smallmatrix} & C \cdot CN \\ & | \\ C \cdot O \cdot CHMe \cdot CO \cdot NH_2 \end{smallmatrix}$, crystallises in thin needles, melts at 170.5°, and has $[a]_D + 93.02^\circ$. The *acid*, similarly obtained from *lævo*-ethyl α -cyanocamphorpropionate, melts at 85°, has $[a]_D + 13.43^\circ$, forms an *ammonium*, a *silver*, and a *copper* salt; the *amide* forms beautiful white needles soluble in benzene, ether, light petroleum, or chloroform, melts at 183°, and has

$[\alpha]_D + 75.20^\circ$. *Ethylcyanocamphorisobutyrate*, $C_8H_{14} \begin{smallmatrix} \diagup C \cdot CN \\ | \\ C \cdot O \cdot CMe_2 \cdot CO_2Et' \end{smallmatrix}$ is an oil boiling at $220-226^\circ$ under 18 mm. pressure. M. A. W.

Transformation of Carvone into α -Phellandrene. CARL D. HARRIES and MANUEL JOHNSON (*Ber.*, 1905, 38, 1832—1835).—Wallach has shown (*Abstr.*, 1904, i, 1035) that the suitable reduction of active nitrophellandrene yields $\Delta^{5,6}$ -menthene-2-one; by converting the latter into α -phellandrene the author now renders it possible to transform carvone into α -phellandrene.

Chlorophellandrene, $CMe \begin{smallmatrix} \diagup CCl : CH \\ | \\ CH \cdot CH_2 \end{smallmatrix} > CHPr^s$, obtained by the action of phosphorus pentachloride on Δ^6 -menthene-2-one, is a colourless, highly refractive oil with a faint ethereal odour, and has $\alpha_D - 28^\circ$ in a decimeter tube at 20° . On reduction with zinc dust in methyl-alcoholic solution and in an atmosphere of nitrogen, it is converted into α -phellandrene.

Δ^6 -Menthene-2-amine, $CMe \begin{smallmatrix} \diagup CH(NH_2) \cdot CH_2 \\ | \\ CH \cdot CH_2 \end{smallmatrix} > CHPr^s$, obtained by reducing the oxime of Δ^6 -menthene-2-one with zinc dust and acetic acid, is a colourless oil which boils at 89° under 14 mm. pressure, has a basic, camphor-like odour, $n_D 1.47957$ at 20° , sp. gr. 0.8896 at 20° , and $\alpha_D + 104.40'$ in a decimetre tube at 20° . Its *hydrochloride* melts at 188° . On treating the base with phosphoric acid and distilling the phosphate in a vacuum, a hydrocarbon is obtained which is probably α -phellandrene. T. H. P.

Essential Oil of *Achillea Nobilis*. P. ECHTERMEIER (*Arch. Pharm.*, 1905, 243, 238—246).—The oil examined was obtained from *Achillea nobilis* when flowering; it had sp. gr. 0.9353 at 15° and rotation -20.82° in a 200 mm. tube, and boiled at $170-265^\circ$, the three fractions collected containing C 84—79 and H 11.4—10.7 per cent.; the ester number corresponded with 18 per cent. of $C_{10}H_7 \cdot OAc$, the acetyl number with 13 per cent. of $C_{10}H_7 \cdot OH$.

No oxime could be obtained from the oil. When some of it was allowed to fall gradually on to phosphoric oxide, the mixture being cooled, and the product distilled and then redistilled repeatedly over sodium, camphene was obtained together with an oil which also had the composition $C_{10}H_{16}$; this oil boiled at $171-177^\circ$.

When the crude oil was boiled with alcoholic potassium hydroxide, decolic, acetic, and formic acids seemed to be present among the products. Small quantities of a phenol were also present. Further products were borneol; an oil which also had the composition $C_{10}H_{18}O$, boiled at $197-201^\circ$, and had an odour resembling that of linalool; and an oil which boiled at $248-265^\circ$, had the composition $C_{10}H_{16}O$, and yielded, when distilled repeatedly over sodium, camphene and an oil which boiled at $240-245^\circ$ and had the composition $C_{10}H_{16}$, resembling in these respects the less volatile fractions of oil of camomile and of other essential oils. C. F. B.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Centr.*, 1905, i, 1469—1471; from Schimmel's *Geschäftsber.*, April, 1905. Compare Abstr., 1903, i, 185; 1904, i, 603).—Para copaiva balsam yields 62.5 per cent. of a yellow oil, which is soluble in 7.5—8 volumes of 95 per cent. alcohol and has a sp. gr. 0.9180 at 15°, α_D - 78°48', n_D 1.50096 at 20°, acid number 3.14, and ester number 0. From Bahia and Angostura copaiva balsams, 61.93 and 52.3 per cent. respectively of slightly yellow oils are obtained. The former has a sp. gr. 0.8982 at 15°, α_D - 9°37', n_D 1.49460, acid number 7.87, and saponification number 9.82; it dissolves in 8—10 volumes of 95 per cent. alcohol, forming a slightly turbid solution. The Angostura oil is soluble in 5.5 volumes of 95 per cent. alcohol; it has a sp. gr. 0.9161 at 15°, α_D - 2°20', n_D 1.50169 at 20°, acid number 10.89, and ester number 0.

Cypress oil distilled from fresh material in the South of France is soluble in 5—6 volumes of 90 per cent. alcohol; it has a sp. gr. 0.868—0.878 at 15°, α_D + 22° to + 31°, acid number 0, and ester number 5—10. The acetyl derivative has ester number 10—15. The oil distilled in Germany dissolves in 2—6 volumes or more of 90 per cent. alcohol; it has a sp. gr. 0.88—0.892 at 15°, α_D + 4° to + 18°, acid number 1.5—3, and ester number 15—22 (acetyl derivative 43—49). The oil obtained from the fruit is similar to the ordinary French oil, and is soluble in 6 volumes or more of 90 per cent. alcohol; it has a sp. gr. 0.8686 at 15°, α_D + 30°48', acid number 0, and ester number 6.74 (acetyl derivative 11.78).

Bergamot oil is chiefly adulterated with lemon oil or the terpenes of lemon oil; the addition of these substances is indicated by the increased rotatory power of the oil.

The bright yellow oil from *Eucalyptus polybractea* closely resembles that of *Eucalyptus odorata*, and contains a considerable quantity of cineol; it has a sp. gr. 0.9193 at 15° and α_D - 1°3', and smells strongly of cuminaldehyde.

Further examination of ginger grass oil has shown that it cannot be an inferior Palma rose oil; but is probably derived from a plant which closely resembles *Andropogon Schoenanthus*. The dihydrocuminol, $C_{10}H_{16}O$ (*Geschäftsber.*, October, 1904; Walbaum and Hüthig, Abstr., 1905, i, 53), obtained from this oil, when reduced with sodium amalgam, yields a tetrahydrocuminol, $C_{10}H_{18}O$, which boils at 216—218° or at 79—80° under 5 mm. pressure and has a sp. gr. 0.9419 at 15°; the phenylurethane compound melts at 85—86°. When oxidised with potassium dichromate and sulphuric acid, it forms *dihydrocuminolaldehyde*, $C_{10}H_{14}O$, and *dihydrocuminic acid*. The former boils at 235° under 755 or at 85° under 4 mm. pressure; it has a sp. gr. 0.9698 at 15°, α_D - 37°54', and n_D 1.50702 at 20°. The semi-oxamozone melts at 228°. *Dihydrocuminic acid*, $C_{10}H_{14}O_2$, melts at 130—131° and yields a *dibromide* and a *hydrobromide* which melt at 167—168° and 175° respectively; it is not identical with the acid obtained by Villiger and von Baeyer from nopinic acid. When cautiously heated with nitric acid, it forms cuminic acid, but when added to cold concentrated nitric acid it yields 3-nitrocuminic acid.

Inactive carvone has been found in ginger grass oil and methyl-

heptenone in Palma rose oil. A sample of hop oil was found to be adulterated with Gurjun balsam oil. The hydrochloride of *isosafrole*, prepared by passing dry hydrogen chloride into *isosafrole*, contains 1 mol. HCl and reacts with sodium methoxide, ethoxide, or amyloxyde. The *methoxy*-compound boils at 110—112° under 5 mm. pressure and has a sp. gr. 1.1116 at 15° and n_D 1.51619 at 15°. The *ethoxy*-compound boils at 110—111° under 3.5 mm. pressure, and has a sp. gr. 1.0796 at 15° and n_D 1.50884 at 15°. The *amyloxy*-compound boils at 136—137° under 13.5 mm. pressure, and has a sp. gr. 1.0258 at 15° and n_D 1.49775 at 15°. By the action of water at a high temperature, or of dilute acids on these compounds, the alcohol appears to be regenerated, but strong alkalis have no action. By the action of phosphorus pentachloride on the methoxy-compound and treatment of the product with water, a compound, $C_{10}H_8O_3$, is formed, which is possibly the 1:3:4-allylcatechol ester of carbonic acid; it has an odour slightly resembling that of coumarin, melts at 84.5—85°, and boils at 130—135° under 3.5 mm. pressure. When treated with acetic acid according to Bertram's method, combination does not take place at the double linking, but a substance is formed which is probably a polymeric *isosafrole*; it melts at 90—91° and boils at 220° under 3 mm. pressure. *isoSafrole* itself reacts with phosphorus pentachloride, forming a product which, when boiled with a strong solution of potassium hydroxide in alcohol, yields the ketone, $CH_2O_2 \cdot C_6H_3 \cdot COEt$, melting at 39°.

Small quantities of a base which has a narcotic odour have been found in oil of caraway, together with dihydrocarvone and dihydrocarveol. The base boiling at 135—140° under 3—4 mm. pressure, which was found in patchouli oil (Abstr., 1904, i, 604), forms a *hydrochloride*, $C_{14}H_{23}ON \cdot HCl$, which melts at 147.5—148.5°; the *platinichloride* melts at 175°.

The oil from the wood of *Fagara octandra*, a Mexican *Rutaceae*, is bright yellow and has an odour which resembles that of linalool; it has a sp. gr. 0.922 at 15°, $n_D + 2^\circ 30'$, and ester number 6.09. *Inula graveolens* yields a brown oil, which has a green fluorescence and probably contains bornyl acetate; it has a sp. gr. 0.9754 at 15°, $n_D - 36^\circ 40'$, acid number 8.45, and ester number 161.3 (acetyl derivative 239.38). The oil prepared from the leaves of *Cupressus Lambertiana* is yellowish-green and has an odour similar to that of balm; it has a sp. gr. 0.8656 at 15°, $n_D + 31^\circ 53'$, acid number 1.5, and ester number 13.9 (acetyl derivative 50.82). The leaves of *Laurus Camphora*, distilled in Cannes, yielded about 0.52 per cent. of a colourless oil, which has an odour similar to that of cardamom. Pinene, cineol, *l*-terpineol, and probably camphene are contained in this oil; it has a sp. gr. 0.9058 at 15°, $n_D - 26^\circ 12'$, acid number 0.34, and ester number 8.82 (acetyl derivative 46.9). About 0.76 per cent. of a brownish-yellow oil was distilled from the fruit of *Amomum mala* in Amani (German E. Africa); it contains a considerable quantity of cineol, together with *terpineol*, and has a sp. gr. 0.9016 at 15°, $n_D - 10^\circ 46'$, acid number 3.5, and ester number 1.7 (acetyl derivative 67.05). Vetiver oil, prepared from the fresh roots, is bright brown, and has a sp. gr. 1.0023 at 15°, $n_D + 33^\circ 42'$, acid number 16.06, and ester number

12.16 (acetyl derivative 142.35). The balsam of *Hardwickia binata* (oil of Ennaikulavo), when distilled with steam, yields about 44 per cent. of a colourless, rather limpid oil, which has a sp. gr. 0.9062 at 15°, $\alpha_D - 7^\circ 42'$, acid number 0.85, and ester number 2.88. Bay berries from the Bermudas yield 3.66 per cent. of a yellowish-brown oil, which has a sp. gr. 1.0170 at 15° and $\alpha_D - 7^\circ 3'$; it contains 73 per cent. of phenols. Eugenol and *l*-phellandrene were isolated, but probably not myrcene. About 0.29 per cent. of a lemon-yellow oil may be obtained from *Artemisia annua*; it has a sp. gr. 0.8912 at 15°, $\alpha_D - 1^\circ 18'$, acid number 3.8, and ester number 19.2 (acetyl derivative 44.5). The bark of *Tetranthera polyantha* var. *citrata* yields 0.81 per cent. of a lemon-yellow oil, which probably contains citral and citronellal, and has a sp. gr. 0.8904 at 15° and $\alpha_D + 10^\circ 11'$, whilst from the leaves 5.42 per cent. of a bright yellow oil is obtained, which contains citral and cineol and has a sp. gr. 0.9042 at 15° and $\alpha_D 15^\circ 41'$.

The quantitative determination of aldehydes and ketones by means of a saturated solution of sodium sulphite gives very good results for carvone and pulegone, and is also satisfactory for citral and cinnamaldehyde, but not for citronellal. Benzaldehyde, anisaldehyde, and cuminaldehyde cannot be estimated by this method. E. W. W.

Euphorbium. ALEXANDER TSCHIRCH and PAUL (*Arch. Pharm.*, 1905, 243, 249—291).—Some difficulty was experienced in obtaining a sample of the resin fairly free from vegetable and earthy impurities. The specimen examined had acid number 36—39, saponification number 80—110, methyl number 1.68. The following percentages were soluble in the solvents named: alcohol (of 50, 60, 75, 90, 96 per cent. by volume respectively), 34, 44, 50, 62, 74—75; ether, 56; acetone, 80; chloroform, 60; ethyl acetate, 62; toluene, 62; amyl alcohol, 74; carbon disulphide, 88; light petroleum, 36; acetic acid, 96; water, 32.5. The part soluble in ether had acid number 40, and saponification number 100; that soluble in alcohol had acid number 19. The ash amounted to 4.1 per cent. when ignited over the blow-pipe, to 8 per cent. when heated over the bunsen burner; it consisted mainly of calcium oxide or carbonate respectively. The crude resin contains a trace of nitrogen, but the purified resin contains none. When a filtered light petroleum extract of the resin is floated on a solution of one drop of concentrated sulphuric acid in 20 c.c. of water, a very stable blood-red layer is formed at the surface where the two liquids touch; on shaking, the whole of the acid liquid becomes red, and this colour only slowly changes to brown. The reaction may be used for purposes of identification; an extract of the most suitable concentration is obtained from 0.1 gram of euphorbium and 10 c.c. of light petroleum.

From an ethereal solution of the resin, 1 per cent. aqueous ammonium carbonate extracts *euphorbic acid*, $C_{24}H_{30}O_6$, which is amorphous, melts at 107—108°, and has acid number 130—135, corresponding with monobasicity, and saponification number 204.

From the residual ethereal solution, no appreciable amount of anything was extracted by 1 per cent. aqueous sodium carbonate or sodium hydroxide.

Concentrated aqueous sodium hydrogen sulphite extracted a very small quantity, about 0.005 per cent., of a substance which melted at 126° and gave several of the reactions of an *aldehyde*.

The ethereal solution remaining was evaporated; the residue was freed from euphorbone by extraction with light petroleum, mixed with aqueous potassium hydroxide, and distilled with steam for weeks. The aqueous distillate contained practically nothing, so that no essential oil can have been present. Undissolved, there remained a small quantity of *euphorboresen*, $C_{33}H_{45}O_4$, which is amorphous and melts at $74-76^{\circ}$. When the residual alkaline liquid was acidified, α -*euphorboresen*, $C_{38}H_{48}O$, was precipitated as an amorphous substance melting at about 75° and now insoluble in dilute aqueous potassium hydroxide; the liquid still contained a small quantity of a substance with the character of a *phenol*.

From an aqueous extract of the drug, calcium malate was isolated; also a dextrorotatory *carbohydrate* that was precipitated by alcohol, and another (pentosan?) which remained dissolved. No appreciable amount of any gum was present. Nor could tartaric, citric, or oxalic acid be detected.

Grains of starch were isolated from the drug; these had the shape of dumb-bells or bones, as often happens with the *Euphorbiaceae*. An amorphous, pungent principle could be extracted from the drug with water, alcohol, or ether.

Euphorbone, $C_{30}H_{48}O$ (molecular weight found 501—517), is best obtained from the drug by extraction with light petroleum and crystallisation first from alcohol and then repeatedly from acetone. It melts at $115-116^{\circ}$ and distils and sublimes unchanged under diminished pressure; from light petroleum, it crystallises with some of the solvent, and then melts at $67-68^{\circ}$. It is optically inactive; it does not contain methoxyl or ethoxyl groups, and its iodine number, 101—112, suggests that addition and substitution occur together. Attempts to prepare an acetyl or a benzoyl derivative were unsuccessful. Alcoholic potassium hydroxide is without action, and fusion with potassium hydroxide leads to no definite result. By heating euphorbone with nitric acid of sp. gr. 1.34, an amorphous, yellow *substance* was obtained with the composition $C_{27}H_{51}O_7(NO_2)_2$.

In 100 parts of the drug were found: euphorbic acid, 0.7; euphorbone, 40, and amorphous resens, 21; malates, 25, and carbohydrate, 2; impurities and loss, 11.

C. F. B.

Pentose Reactions of Saponins. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1905, 243, 247—248).—By means of the phloroglucinol and orcinol reactions, furfuraldehyde has been detected after the following saponins have been boiled with dilute hydrochloric acid (compare Plzák, *Abstr.*, 1903, i, 643). Saponin from *Gypsophila spec.*, *Camellia theifera*, *Polygala senega* (senegin), *Acacia concinna*, *Entada scandens*, *Dialopsis africana*, *Digitalis purpurea* (digitonin), *Guaiacum off.*; saponic acid from *Quillaia saponaria* (quillaic acid) and *Guaiacum off.*, and sapotoxin from *Quillaia saponaria*. These substances must therefore yield pentoses on hydrolysis, and are to be regarded as pentosides.

No furfuraldehyde could be detected in the case of the saponin from *Verbascum sinuatum* and the three from *Sarsaparilla*. C. F. B.

Chlorophyll. LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, **44**, 422—426).—The optical activity of chlorophyll and its derivatives is believed to be due to the green constituent. Hartley's blue chlorophyll is considered to be unchanged chlorophyll. W. D. H.

Oxidation of the Higher Homologues of Aniline on the Fibre. S. KIRPITSCHNIKOFF (*Zeit. Farb. Text. Ind.*, 1905, **4**, 233—234).—The following bases, printed on a fabric, may be oxidised to a moderately permanent dye by means of sodium chlorate and potassium ferrocyanide; the colour of the dye is shown in brackets. Aniline (black); *o*-toluidine (dark violet); *m*-toluidine (blackish-violet); *p*-toluidine (chestnut-brown); xyldine (black); cumidine (brown with a rose shade). W. A. D.

Brown Sulphur Dye from 2:4:5-Triaminotoluene. KALLE & Co. (D.R.-P. 157540).—When fused with sodium sulphide and sulphur at 160°, 2:4:5-triaminotoluene yields a remarkably fast brown dye. In place of triaminotoluene, the more readily accessible benzeneazo-*m*-tolylenediamine may be employed; in this case, the product is afterwards heated at 220° to remove aniline. C. H. D.

Sulphur Dye from 2:2'-Diamino-4:4'-oxalotoluidide. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 157103).—A yellow dye resembling that obtained by fusing 2:2'-diamino-4:4'-oxalotoluidide with sulphur (this vol., i, 249), but having greater fastness towards alkalis, may be prepared by melting the diamino-oxalotoluidide with 2 mols. of *m*-tolylenediamine at 150—200° and fusing the product with sulphur at a temperature above 170°. C. H. D.

Derivatives of Dihydroisobenzofuran. ALFRED GUYOT and J. CATEL (*Compt. rend.*, 1905, **140**, 1348—1350. Compare this vol., i, 226).—When phenylphthalide is added to a solution of magnesium phenyl bromide in ether, there is formed *o*-benzhydryltriphenylcarbinol, $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}\cdot\text{OH}$, but when the two reagents are mixed in the reverse order there is obtained 2-hydroxy 1:2-diphenyl-1:2-dihydroisobenzofuran, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CHPh} \\ \text{CPh}(\text{OH}) \end{smallmatrix}\rangle\text{O}$, which forms small, colourless crystals, dissolves in organic solvents, and readily loses a mol. of water when heated alone or when boiled in acetic acid or in alcohol containing some hydrogen chloride, yielding a substance which crystallises in golden-yellow leaflets, melts at 125°, and dissolves in benzene with a green fluorescence. This new substance, on reduction with sodium amalgam, furnishes 1:2-diphenyl-1:2-dihydroisobenzofuran (m. p. 96°), and is oxidised by potassium dichromate in acetic acid to *o*-dibenzoylbenzene, whence the authors conclude that it has the constitution $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CPh} \\ \text{CPh} \end{smallmatrix}\rangle\text{O}$ or $\text{C}_6\text{H}_4\ll\begin{smallmatrix} \text{CPh} \\ \text{CPh} \end{smallmatrix}\rangle\text{O}$.

o-Dibenzoylbenzene yields a diphenylhydrazone melting at 165° and

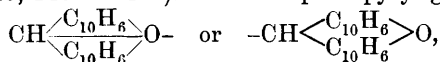
a *phthalazine*, $C_6H_4 \begin{smallmatrix} \text{CPh:N} \\ \text{CPh:N} \end{smallmatrix}$, which melts at 192° and is soluble in acids, and furnishes a crystalline *platinichloride*. When either 2-hydroxy-1:2-diphenyl-1:2-dihydroisobenzofuran or *o*-dibenzoylbenzene is reduced with sodium amalgam, *o*-dibenzhydrylbenzene,



is produced. This melts at 128° and, when heated in acetic acid solution with hydrochloric acid, yields the 1:2-diphenyl-1:2-dihydroisobenzofuran mentioned above.

T. A. H.

Basicity of Pyronic Oxygen. Halogen Double Salts of Metals and Dinaphthapyryl. ROBERT FOSSE and L. LESAGE (*Compt. rend.*, 1905, 140, 1402—1403).—The dinaphthapyryl group,



has basic properties, and a number of halogen double salts have been prepared in which this group plays the rôle of an atom of an alkali metal. The formulæ of the double chlorides and bromides are given below, the dinaphthapyryl group being represented by R.

AuCl₃, RCl, microscopic red crystals.
HgBr₂, RBr, red, yellow by reflected light.
CuBr₂, RBr, green.
FeBr₃, RBr, red, yellow by reflected light.

PtCl₄, 2RCl,
PtCl₂, 2RCl, green crystals.
CdBr₂, 2RBr, red, green in reflected light.
MnBr₂, 2RBr, red, yellow in reflected light.
CoBr₂, 2RBr, red, metallic shimmer.

The double salts are represented as containing quadrivalent basic oxygen corresponding with the first formula for the dinaphthapyryl group.

H. M. D.

Origin of Alkaloids in Plants. AMÉ PICTET (*Arch. Sci. phys. nat.*, 1905, [iv], 19, 329—352).—The alkaloids in the plant economy correspond with the urea, uric acid, glycine, &c., in the animal system. They are localised in special tissues and are the nitrogenous products of cell metabolism arising from the breaking down of more complex substances and subsequent chemical modification by condensation with other compounds present in the plant, the most common of these changes being the methylation of possibly noxious hydroxyl or imino-groups by means of formaldehyde according to the equations $R \cdot OH + CH_2O = R \cdot OMe + O$; $R \cdot NH + CH_2O = R \cdot NMe + O$; $R(OH)_2 + CH_2O = R \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} CH_2 + H_2O$ (Eschweiler, this vol., i, 328). The alkaloids containing the pyrrole or indole ring (nicotine, atropine, cocaine, hygrine, strychnine, or brucine) are degradation products of proteids (Fischer, Abstr., 1901, i, 745, 780; Nencki, Abstr., 1901, i, 434, 554), but the pyridine, piperidine, or quinoline ring characteristic of the alkaloids of hemlock, quinine, opium, &c., does not occur in proteids, nucleins, lecithins, or any other complex vegetable product, and the author is of opinion that these rings are formed by an intramolecular transformation of a methylated pyrrole or indole ring; such

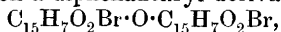
transformations can be effected by the action of heat, the author having obtained pyridine from 1-methylpyrrole or 2-methylpyrrole; quinoline from 1-methylindole; *isoquinoline* from methylphthalimidine, and phenanthridine from methylcarbazole (compare Abstr., 1904, i, 771).
M. A. W.

Aminocodeine. EDUARD VONGERICHTEN and CARL WEILLINGER (*Ber.*, 1905, 38, 1857—1859).—The *methiodide*, $C_{18}H_{20}O_5N_2, MeI$, is formed by boiling nitrocodeine with methyl iodide in methyl-alcoholic solution; when boiled with 25 per cent. aqueous sodium hydroxide, it forms nitromorphimethine, $C_{19}H_{22}O_5N_2$, which crystallises in yellow needles and melts at 214—215°. The *methiodide*, $C_{19}H_{22}O_5N_2, MeI$, crystallises in yellow needles.

When reduced with tin and glacial acetic acid, nitrocodeine forms *diacetylaminocodeine*, $C_{22}H_{26}O_5N_2$, which crystallises in flat, white needles, melts at 120°, and forms the *methiodide*, $C_{22}H_{26}O_5N_2, MeI$. This crystallises in white needles, melts at 251—252°, and when boiled with silver acetate and acetic anhydride, the reaction mixture being afterwards heated in a sealed tube at 160—170°, forms *triacetylaminomethylmorphol*, $C_{21}H_{21}O_5N$, which crystallises in yellow needles, melts at 178—179°, and dissolves in alcoholic sodium hydroxide to a brown solution. Oxidation of the triacetyl compound leads to the formation of a *quinone* which contains nitrogen; it is obtained as a yellow precipitate on addition of sulphuric acid to its solution in aqueous sodium hydrogen sulphite, and dissolves in alcoholic sodium hydroxide to a green solution which becomes red on addition of acetic acid. On solution of the quinone in aqueous sodium hydroxide and precipitation with acetic acid, the *amino-quinone* is obtained as a dark blue, flocculent substance which dissolves in alcohol or chloroform to red solutions. A *substance* which crystallises in red needles, melts at 240°, and dissolves in concentrated sulphuric acid, or in alcoholic sodium hydroxide to red solutions, is formed as a by-product in the oxidation of the triacetyl compound.

The properties of the quinone show that the nitro-group of nitrocodeine must have replaced a hydrogen atom of the phenanthrene diphenyl nucleus.
G. Y.

Derivatives of Morphenol. EDUARD VONGERICHTEN (*Ber.*, 1905, 38, 1851—1857. Compare Abstr., 1898, i, 98; Abstr., 1901, i, 742).—*α*-Bromomorphenol methyl ether, obtained as previously described from bromomethylmorphimethine, the *methiodide* of which melts at 252°, yields on oxidation a diphenanthryl derivative,



melting at 330°, and a small amount of a bromo-quinone which forms condensation products with *o*-diamines.

β-Bromomorphenol methyl ether is formed by the action of bromine on acetylmorphenol and hydrolysis of the acetylbromomorphenol (m. p. 208°) by means of sodium methoxide in a sealed tube at 100°. Both bromomorphenol methyl ethers melt at 124°, but a mixture of the two melts at 95—98°. Oxidation of the *β*-bromo-ether with chromic acid in glacial acetic acid solution leads to the formation of reddish-

brown amorphous products and not to a crystalline quinone, whereas by the oxidation of acetyl bromomorphenol there is obtained a *bromo-morphenolquinone*, which dissolves in aqueous sodium hydroxide to a carmine solution and condenses with *o*-tolylenediamine to a yellow, crystalline *azine*, $C_{23}H_{13}O_3N_2Br$. The action of bromine on the α -bromoether leads to the formation of a *dibromomorphenol methyl ether*, $C_{15}H_9O_2Br_2$, which crystallises in needles and melts at 203° ; with bromine in carbon disulphide solution, the β -bromo-ether forms an *additive* compound, which separates in nodular crystals and, when heated at 105 – 120° , loses hydrogen bromide and forms a *dibromo-morphenol methyl ether*, melting at about 200° . G. Y.

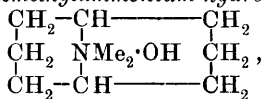
1-Methylpyrrolidine from Nicotine. AMÉ PICTET (*Ber.*, 1905, **38**, 1951–1952).—By the action of silver oxide on nicotine, at least three other substances are formed in addition to nicotyrine, and these may be separated from one another and from unchanged nicotine by distillation in a vacuum.

The first fraction consisted of 1-methylpyrrolidine, which boils at 81 – 82° , has an odour of piperidine, and is strongly alkaline. It was further identified by means of its aurichloride, hydrochloride, and picrate respectively. A. McK.

Reduction of Metan nicotine with Sodium and Absolute Alcohol. EMIL MAASS (*Ber.*, 1905, **38**, 1831–1832).—*Hexahydro-metan nicotine*, $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{NH} \cdot \text{CH}_2 \end{smallmatrix} > CH \cdot CH : CH \cdot CH_2 \cdot CH_2 \cdot NHMe$, obtained by reducing metan nicotine by means of sodium and absolute alcohol, is an optically inactive, clear oil, which boils at 251 – 252° , has a sp. gr. 0.944 at 15° , is readily soluble in ether, and has an odour closely resembling that of piperidine. T. H. P.

Some Derivatives of ψ -Pelletierine. RICHARD WILLSTÄTTER and HANS VERAGUTH (*Ber.*, 1905, **38**, 1984–1991).—*n*-Methylgranatanine, prepared by Piccinini's method (*Abstr.*, 1898, i, 488), melts at 55 – 58° and is apparently purer than Ciamician and Silber's base (*Abstr.*, 1894, i, 154), which melted at 49 – 50° ; the *platinichloride* forms short prisms and melts and decomposes at 220 – 221° .

N-Methylgranataninemethylammonium hydroxide,

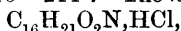


prepared from the corresponding methiodide by means of silver oxide, crystallises in hard, rectangular, efflorescent plates, containing about $16H_2O$. On distilling, the ammonium base loses water giving

Δ^1 -des-dimethylgranatanine, $CH_2 \begin{smallmatrix} CH_2 \cdot CH(NMe_2) \cdot CH_2 \\ CH_2 \cdot CH : CH - CH_2 \end{smallmatrix}$, which is a colourless oil with a narcotic odour and boils at 89.5 – 92° under 14.5 mm. pressure; it has a sp. gr. 0.916 at $6^\circ/4^\circ$. The *picrate* forms flat prisms and melts at 155° ; the *platinichloride* forms slender needles and melts and decomposes at 178 – 180° ; the *methiodide*

crystallises from alcohol in long needles and melts and decomposes at 264° .

In addition to *N*-methylgranatanine, the electrolytic reduction of ψ -pelletierine gives rise to a mixture of ψ -methylgranatoline (Ciamician and Silber's methylgranatoline) and a new base, stereoisomeric with the latter, which is called *methylgranatoline*, on account of its appearing more closely analogous with tropine than is Ciamician and Silber's compound; it crystallises from light petroleum in prisms, melts at 69 — 70° , is more hygroscopic and more soluble in light petroleum than ψ -methylgranatoline, and is easily oxidised by potassium permanganate to ψ -pelletierine. It is transformed into ψ -methylgranatoline by boiling with sodium amyloxide solution. Methylgranatoline *aurichloride* forms sheaves of prisms and melts and decomposes at 210 — 211° . The *hydrochloride*,

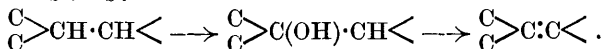


of the benzoyl derivative of methylgranatoline crystallises from alcohol in nodular aggregates of needles and melts at about 182° . The *benzoyl* derivative of ψ -methylgranatoline forms reticular aggregates of needles and melts at 34° ; its *hydrochloride* forms rhombohedra melting at 235° and its *hydriodide* crystallises in prisms melting at 242 — 243° .

des- ψ -*Dimethylgranatoline*, $\text{OH}\cdot\text{C}_8\text{H}_{12}\cdot\text{NMe}_2$, obtained by the "exhaustive" methylation of ψ -methylgranatoline, boils at 141 — 142° under 13.5 mm. pressure; it is accompanied by an *isomeride*, $\text{C}_{10}\text{H}_{19}\text{ON}$, which boils at 113 — 115° under 16.5 mm. and at 234.5 — 238.5° (corr.) under the ordinary pressure. The nature of the latter is uncertain, but its behaviour on benzoylation shows that it contains a hydroxyl group. 3-*Chloro- ψ -methylgranatanine*, $\text{C}_9\text{H}_{16}\text{NCl}$, obtained by the action of a mixture of phosphorus oxychloride and pentachloride on the alkamine, crystallises from light petroleum in needles, melts at 56° , and boils at 117 — 118° under 18 mm. pressure. 3-*Chlorotropane*, $\text{C}_8\text{H}_{14}\text{NCl}$, prepared similarly from tropine, boils at 105 — 105.5° under 21 mm. pressure.

W. A. D.

Oxidation of Sparteine. RICHARD WILLSTÄTTER and WILHELM MARX (*Ber.*, 1905, 38, 1772—1780. Compare Ahrens, *Abstr.*, 1893, i, 232; 1894, i, 150; 1897, i, 231; and Willstätter and Fournneau, *Abstr.*, 1902, i, 557).—On oxidising sparteine sulphate with an amount of chromic acid corresponding with 6 atoms of oxygen, an unsaturated base, *spartyrine*, $\text{C}_{15}\text{H}_{24}\text{N}_2$, is obtained, which, although having the same composition as Ahrens' dehydrosparteine, differs completely from it; it crystallises from ethyl acetate, melts at 153 — 154° , has $[\alpha]_D - 25.96^{\circ}$ at 18.5° , and gives a hygroscopic *hydrochloride*, $\text{C}_{15}\text{H}_{26}\text{N}_2\text{Cl}_2\cdot\text{H}_2\text{O}$; the *platinichloride*, $\text{C}_{15}\text{H}_{26}\text{N}_2\text{Cl}_6\text{Pt}\cdot 3\text{H}_2\text{O}$, forms orange-yellow needles. As spartyrine contains a double linking, the oxidation of sparteine probably occurs thus:



When double the quantity of chromic acid is used in oxidising sparteine, the principal product is oxysparteine, $\text{C}_{15}\text{H}_{24}\text{ON}_2$, which melts at 87.5° instead of 84° as stated by Ahrens; it boils at 209°

under 12.5 mm. pressure, has $[\alpha]_D - 10.04^\circ$ at 18° , and resists the action of potassium permanganate and chromic acid. The *platinchloride*, $C_{15}H_{26}ON_2Cl_6Pt \cdot 2H_2O$, forms short prisms, becomes anhydrous at 130° , and melts and decomposes at $225-227^\circ$; the *mercurichloride* sinters at 150° and decomposes at 195° ; the *thiocyanate* sinters at 80° and melts at 87.5° .

Both spartyrine and oxysparteine are accompanied by another substance, $C_{15}H_{24}O_4N_2$, which cannot be obtained in a crystalline condition, is very hygroscopic, and melts and decomposes at 158° ; when precipitated by adding alcohol to its solution in acetone, it contains $1H_2O$. It can be further oxidised by chromic acid to a substance, $C_{12}H_{22}O_4N_2$, which resembles the compound $C_{15}H_{24}O_4N_2$, but separates from acetone on adding alcohol with $\frac{1}{2}EtOH$. W. A. D.

Pyrogenic Transformation of Methylpyrroles into Pyridine Derivatives. AMÉ PICTET (*Ber.*, 1905, **38**, 1946—1951. Compare Pictet and Steinmann, *Abstr.*, 1904, i, 771).—Pyridine is formed when 2-methylpyrrole is distilled through a tube heated to dull redness. It is probable that the 2-methylpyrrole is an intermediate product in the transformation of 1-methylpyrrole into pyridine. 1-Benzylpyrrole (Ciamician and Silber, *Abstr.*, 1887, 843) may be prepared by the distillation of benzylamine mucate. When passed through a hot tube, it yields 3-phenylpyridine.

A 17 per cent. yield of quinoline is obtained by passing the vapour of 2-methylindole through a hot tube, and a 40 per cent. yield of phenanthridine by treating methylcarbazole in a similar manner.

The base obtained by Graebe and Pictet (*Abstr.*, 1889, 141) by distilling methylphthalimidine with zinc dust is *isoquinoline*. J. J. S.

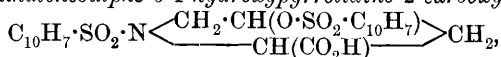
Synthesis of Hydroxypyrrolidinecarboxylic acids (Hydroxyprolines). HERMANN LEUCHS (*Ber.*, 1905, **38**, 1937—1943).—Ethyl δ -chloro- α -bromo- γ -valerolactone- α -carboxylate (Traube and Lehmann, *Abstr.*, 1901, i, 502) reacts with a cold methyl-alcoholic solution of ammonia yielding the *monoamide* of *chloromethyltrimethyleneoxidedicarboxylic acid*, $O \begin{smallmatrix} \diagup C(\text{CONH}_2)_2 \\ \diagdown \end{smallmatrix} \text{CH}(\text{CH}_2\text{Cl}) \text{CH}_2$, which crystallises from hot water in small needles, melts at $218-219^\circ$ (corr.), and is insoluble in chloroform, benzene, or ethyl acetate.

When the chlorobromo-ester is hydrolysed with concentrated hydrobromic acid and then heated at $120-130^\circ$ under reduced pressure, it yields δ -chloro- α -bromo- γ -valerolactone, $\text{CH}_2\text{Cl} \cdot \text{CH} \begin{smallmatrix} \diagup \text{O}-\text{CO} \\ \diagdown \end{smallmatrix} \text{CH}_2 \cdot \text{CHBr}$, as a viscous oil distilling at $156-164^\circ$ (corr.) under 11 mm. pressure. The crude lactone, when left in contact with concentrated aqueous ammonia, yields a mixture of two isomeric 4-hydroxypyrrolidinecarboxylic acids which are most readily separated by means of their *copper* salts. The copper salt, $\text{Cu}(C_5H_8O_3N)_2 \cdot 4H_2O$, of the α -compound forms deep blue crystals sparingly soluble in water and loses its water of crystallisation at 105° . The corresponding acid, α -4-hydroxypyrrolidine-2-carboxylic acid, $\text{NH} \begin{smallmatrix} \diagup \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \diagdown \end{smallmatrix} \text{CH}(\text{CO}_2\text{H}) \text{CH}_2$, crystallises in small, six-sided plates, melts

and decomposes at 261° (corr.) when rapidly heated, and dissolves readily in water and only very sparingly in alcohol. It has a sweet taste, and its aqueous solution has a neutral reaction. The β -naphthalenesulphone derivative, $C_{10}H_7 \cdot SO_2 \cdot N \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} \text{CH}_2$, melts at $186-187^{\circ}$ (corr.).

The copper salt of the *b*-compound, $(C_5H_8O_3N)_2Cu$, is more readily soluble in water, and on the addition of alcohol crystallises in the form of microscopic six-sided, deep blue plates. The *b*-4-hydroxypyrridine (4-hydroxypyrridine-2-carboxylic acid) melts and decomposes at 250° (corr.) and is somewhat less soluble in water or methyl alcohol than the *a*-compound. It has an insipid taste and its aqueous solution has a feebly acid reaction.

Di-β-naphthalenesulpho-b-4-hydroxypyrridine-2-carboxylic acid,



crystallises from organic solvents in minute needles, melts at $181-182^{\circ}$ (corr.), and is practically insoluble in water or ether.

J. J. S.

Purification of Pyridine. LÉONCE BARTHE (*Bull. Soc. chim.*, 1905, [iii], 33, 659—661).—The "pure pyridine" of commerce frequently contains the homologues of this base and ammonia. Agitation of the pyridine with distilled water and a solution of sodium hypobromite converts the pyridine into (1) a colourless, odourless liquid substance, which contains no bromine and boils at $117-121^{\circ}$, and (2) a crystalline brominated compound. Both these products are being further investigated.

Ammonia may be removed from commercial pyridine by shaking it with water and crystalline magnesium hydrogen phosphate, which combines directly with ammonia or the amines to form salts of the type of magnesium ammonium phosphate. Pyridine purified in this way gives only an indefinite wine colour with litmus solution, and consequently titration with standard acid, using litmus as an indicator, may be applied to the estimation of ammonia in pyridine.

T. A. H.

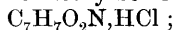
Abnormal Salts of Betaines and Pyridinecarboxylic Acids.

RICHARD TURNAU (*Monatsh.*, 1905, 26, 537—561. Compare Goldschmidt and Hönigschmid, *Abstr.*, 1904, i, 86; ii, 94).—When heated with an excess of methyl iodide, with or without water or alcohol as solvent, in a sealed tube at 100° for 6—7 hours, picolinic acid forms

the methiodide, $\begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{O} \cdot \text{NMe} \\ \text{CH} \cdot \text{CH} \cdot \text{NMeI} \end{smallmatrix} \begin{smallmatrix} \text{CH} \\ \text{C}(\text{CO}_2\text{H}) \end{smallmatrix} \text{CH} \cdot \text{CH}$ which is formed

also by evaporating the methylbetaine of picolinic acid with hydriodic acid. The methiodide crystallises in long, yellow needles, decomposes at $154-158^{\circ}$, is readily soluble in water, but less so in methyl or ethyl alcohol, and is not acted on by boiling water or hydriodic or hydrochloric acid; the potassium salt crystallises in long, hygroscopic needles; the barium salt, $(C_{14}H_{14}O_4N_2I)_2Ba \cdot 4H_2O$, formed by the action of barium carbonate on the methiodide, or of barium iodide on the methylbetaine of picolinic acid, crystallises in white needles, loses

$2\text{H}_2\text{O}$ at 105° , and melts at $130\text{--}150^\circ$. When shaken with freshly precipitated silver chloride in aqueous solution, the methiodide is converted into the *methochloride*, $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N}_2\text{Cl}\cdot\text{HCl}$, which crystallises in needles, sinters at 105° , melts at 120° , is strongly hygroscopic when anhydrous, and when repeatedly evaporated with hydrochloric acid yields the *hydrochloride* of the methylbetaine of picolinic acid,



this decomposes at $165\text{--}170^\circ$. The *methobromide*, $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N}_2\text{Br}\cdot\text{H}_2\text{O}$, formed by the action of silver bromide on the methiodide, melts at 115° , and when evaporated with hydrobromic acid yields the *hydrobromide* of the methylbetaine of picolinic acid, $\text{C}_7\text{H}_7\text{O}_2\text{N}\cdot\text{HBr}$, which crystallises in short, thick needles and decomposes at about 179° .

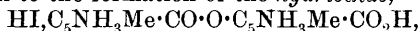
When evaporated with hydriodic acid over the water-bath and finally over sodium hydroxide in a vacuum, picolinic acid forms the *hydriodide*, $\text{HI}\cdot\text{C}_5\text{NH}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_5\text{NH}_3\cdot\text{CO}_2\text{H}$, which crystallises in small, stout, yellow needles, melts and decomposes at $190\text{--}200^\circ$, behaves as a tribasic acid on titration, and when shaken with silver chloride and water yields picolinic acid and its hydrochloride.

The action of methyl iodide on nicotinic acid at 150° leads to the formation of the normal *methiodide* (Meyer, Abstr., 1901, i, 190), which melts at about 220° and, when shaken with silver chloride and water, yields the *methochloride*, $\text{C}_7\text{H}_8\text{O}_2\text{NCl}$; this crystallises in needles or prisms and melts and decomposes at $245\text{--}250^\circ$.

When heated with methyl iodide at 150° for 12 hours, *isonicotinic* acid forms the *methiodide*,

$$\begin{array}{c} \text{CO}_2\text{H}\cdot\text{C}-\text{CH}:\text{CH} \\ | \qquad \qquad | \\ \text{CH}\cdot\text{CH}:\text{NMeI} \end{array} \quad \begin{array}{c} \text{CH}\cdot\text{CH}:\text{NMeI} \\ | \qquad \qquad | \\ \text{CH}\cdot\text{CH}:\text{NMe}\cdot\text{O}\cdot\text{CO}\cdot\text{C}-\text{CH}:\text{CH} \end{array},$$

which crystallises in long, yellow needles or in prisms and plates, melts and decomposes at 247° , and is identical with the intermediate product obtained by Meyer in the preparation of the methylbetaine of *isonicotinic* acid (*Monatsh.*, 1903, 24, 201). The action of methyl iodide on anhydrous 2-methylpyridine-6-carboxylic acid leads to the formation of an *additive compound*, but on the acid containing water of crystallisation to the formation of the *hydriodide*,



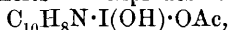
which is formed also by the action of hydriodic acid on 2-methylpyridine-6-carboxylic acid; it melts at 230° . With ethyl iodide, picolinic and *isonicotinic* acids form additive compounds which, when shaken with silver oxide and water, yield the corresponding ethylbetaines. The action of allyl iodide on picolinic acid leads to the formation of the hydriodide, $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_2\cdot\text{HI}$, melting at $190\text{--}200^\circ$.

G. Y.

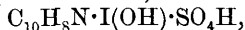
Derivatives of Iodoquinolines with Multivalent Iodine. CONRAD WILLGERODT [and, in part, PAUL FRISCHMUTH] (*Ber.*, 1905, 38, 1805—1811).—8-Iodo-6-methylquinoline, prepared from 8-amino-6-methylquinoline by means of the diazo-reaction, is volatile in steam, crystallises from alcohol in six-sided prisms, and melts at 66° ; the *sulphate*, $\text{C}_{10}\text{H}_8\text{NI}\cdot\text{H}_2\text{SO}_4$, forms yellow needles and melts at 180° ; the *nitrate*, $\text{C}_{10}\text{H}_8\text{NI}\cdot\text{HNO}_3$, melts at 151° ; the *hydrochloride* melts at 216° , the *platinichloride* melts and decomposes at 226° , and the *dichromate*, $2\text{C}_{10}\text{H}_8\text{NI}\cdot\text{H}_2\text{Cr}_2\text{O}_7$, melts at 112° .

6-Methylquinolyl-8-iodinium chloride, $C_{10}H_8N \cdot ICl_2$, obtained by passing chlorine through a solution of 8-iodo-6-methylquinoline in glacial acetic acid, melts and decomposes at 138° .

8-Iodoso-6-methylquinoline, $C_{10}H_8N \cdot IO$, forms a yellowish-white, amorphous powder and melts and explodes at 175° ; the *acetate*,



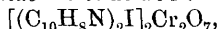
crystallises from glacial acetic acid in slender, colourless needles, darkens at 165° , and melts and decomposes at 186° ; the *nitrate*, $C_{10}H_8N \cdot I(OH) \cdot NO_3$, explodes at 130° , and the *sulphate*,



melts and decomposes at 102° .

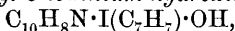
8-Iodoxy-6-methylquinoline, $C_{10}H_8N \cdot IO_2$, separates from water in colourless crystals and explodes violently at 187° .

Di-6-methylquinolyl-8-iodinium hydroxide, $(C_{10}H_8N)_2I \cdot OH$, prepared by the action of silver oxide and water on a mixture of the iodoxy- and iodoso-compounds, was obtained only in solution; the *chloride*, $(C_{10}H_8N)_2ICl$, forms slender, white needles melting at 186° ; the corresponding *bromide* crystallises from dilute alcohol in small needles and melts at 174° , and the *iodide* melts at 162° . The *dichromate*,



decomposes at 190° , the *platinichloride*, $C_{40}H_{32}N_4I_2Cl_6Pt$, at 190° , and the *mercurichloride* melts and decomposes at 144° .

p-Tolyl-6-methylquinolyl-8-iodinium hydroxide,



prepared from p-iodoxytoluene and 2-iodoso-4-methylquinoline, gives the following crystalline salts. The *chloride*, $C_{10}H_8N \cdot I(C_7H_7)Cl$, begins to decompose at 174° and melts at 194° ; the *bromide* melts at 164° , the *iodide* melts and decomposes at 157° , the *dichromate* decomposes at 160° , and the *platinichloride* at 226° .

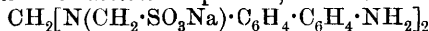
W. A. D.

Dyes from Quinolinium Compounds. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158078).—2-Methylquinoline (quinaldine) combines with alkyl sulphates to form highly hygroscopic methylquinolinium alkyl sulphates. Alkali hydroxides convert these into red or violet dyes, which contain 1 atom of sulphur to 2 mols. of quinaldine, and have active sensitising properties when added to silver haloid emulsions.

2-Methylquinolinium ethosulphate, $C_9NH_6Me \cdot NEt \cdot SO_4Et$, reacts with alcoholic sodium hydroxide, yielding dark red, metallic crystals, soluble in water, alcohol, chloroform, or acetone, insoluble in ether or benzene. Dilute acids dissolve the compound to colourless solutions. 2-Methylquinolinium methosulphate reacts in similar manner.

C. H. D.

Action of Formaldehyde and Sodium Hydrogen Sulphite on Aromatic Diamines. MAURICE PRUD'HOMME (*Bull. Soc. Ind. Mul.*, 1905, 43—44).—When benzidine, dissolved in dilute hydrochloric acid, is added to a mixture of formaldehyde with excess of sodium hydrogen sulphite, a crystalline substance separates, to which the formula

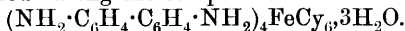


is ascribed. This yields a yellowish-green diazo-compound which combines with phenols, amines, or acids yielding dyes, which

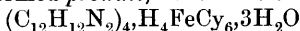
are readily soluble and dye cotton and wool directly (the latter best in an acid bath), and are less sensitive to acids than the corresponding benzidine derivatives. This reaction also takes place with *p*-phenylenediamine, the tolidines, and other aromatic diamines. T. A. H.

Composition of Benzidine Chromate. A. KOTSCHUBEY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 349—351).—The author's analyses of the blue insoluble compound obtained by the action of potassium dichromate on benzidine (compare Julius, *Abstr.*, 1884, 1181) point to its composition being expressed by $C_{12}H_8(NH_2)_2 \cdot CrO_3$. T. H. P.

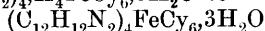
Reaction of Potassium Ferricyanide with Aromatic Polyamines. JACOB N. BARSILOWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 337—348).—When dilute aqueous or aqueous-alcoholic solutions of benzidine and potassium ferrocyanide are mixed, a blue, insoluble compound is formed having the composition



This compound is produced by the action of the oxygen from the water present on the first-formed product, which has the formula



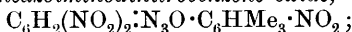
and is a colourless substance; when treated with acids or alkalis, this latter is decomposed into hydroferrocyanic acid and benzidine. The oxidation of $(C_{12}H_{12}N_2)_4 \cdot H_4FeCy_6 \cdot 3H_2O$ to



by air and water is not complete but may be made so by the addition of hydrogen peroxide. T. H. P.

Picryl-, *o-p*-Dinitrophenyl-, and 5-Chloro-2-nitrophenyl-2:4:5-trimethylphenylhydrazines and their Derivatives. CONRAD WILLGERODT and FRANZ HERZOG (*J. pr. Chem.*, 1905, [ii], **71**, 385—398).—*s-Picryl-ψ-cumylhydrazine*, $C_6H_2(NO_2)_3 \cdot NH \cdot NH \cdot C_6H_2Me_3$, is formed by the action of picryl chloride on 2:4:5-trimethylphenylhydrazine-*ψ*-cumylhydrazine in alcoholic solution at 157.5°, is easily soluble in chloroform, benzene, or carbon disulphide, and is oxidised by chromic acid in cold glacial acetic acid solution to *ψ-cumeneazo-2:4:6-trinitrobenzene*, $C_6H_2Me_3 \cdot N_2 \cdot C_6H_2(NO_2)_3$, which crystallises in long, brown needles, and melts at 168°. When boiled with glacial acetic acid, picryl-2:4:5-trimethylphenylhydrazine yields *ψ-cumeneazo-imino-4:6-dinitrobenzene oxide*, $C_6H_2(NO_2)_2 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NO \end{smallmatrix} \cdot N \cdot C_6H_2Me_3$, which

crystallises in golden needles, melts at 222°, and, when nitrated with concentrated nitric acid in concentrated sulphuric acid solution at 0°, forms *nitro-ψ-cumeneazoiminodinitrobenzene oxide*,

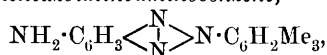


this separates as a yellow, crystalline powder and melts and decomposes at 237°. When boiled with potassium iodide in glacial acetic acid solution in a reflux apparatus, *ψ-cumeneazoiminodinitrobenzene oxide* is reduced to *ψ-cumeneazoiminodinitrobenzene*, $C_6H_2(NO_2)_2 \cdot N_3 \cdot C_6H_2Me_3$, which is obtained as a yellow powder, melting at 151°, and dissolving in boiling dilute sodium hydroxide to a yellow solution.

p-Dinitrophenyl-*ψ*-cumylhydrazine, $C_6H_3(NO_2)_2 \cdot N_2H_2 \cdot C_6H_2Me_3$,

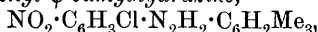
formed by the action of 6-chloro-1:3-dinitrobenzene on ψ -cumylhydrazine in concentrated alcoholic solution, crystallises in matted, yellow needles and melts and decomposes at 198°. ψ -Cumeneazo-2:4-dinitrobenzene crystallises in brown needles and melts at 177—178°.

ψ -Cumeneazoiminonitrobenzene oxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{N}^- \\ | \\ \text{NO} \end{smallmatrix} \right\rangle \text{N} \cdot \text{C}_6\text{H}_2\text{Me}_3$, crystallises in thick, yellow leaflets and melts at 185°. ψ -Cumeneazoiminonitrobenzene, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} \right\rangle \text{N} \cdot \text{C}_6\text{H}_2\text{Me}_3$, crystallises in slender needles, melts at 136·5°, is insoluble in dilute alkali hydroxides, and is reduced by iron and acetic acid or by stannous chloride and hydrochloric acid to ψ -cumeneazoiminoaminobenzene,



which crystallises in brown, transparent leaflets and melts at 147—148°; the hydrochloride, $\text{C}_{15}\text{H}_{16}\text{N}_4 \cdot \text{HCl}$, melts and decomposes at 247·5°; the sulphate, $(\text{C}_{15}\text{H}_{16}\text{N}_4)_2 \cdot \text{H}_2\text{SO}_4$, forms white needles; the platinichloride, $(\text{C}_{15}\text{H}_{16}\text{N}_4)_2 \cdot \text{H}_2\text{PtCl}_6$, forms an amorphous, yellow powder.

5-Chloro-2-nitrophenyl- ψ -cumylhydrazine,



is formed by the action of 1-chloro-3:4-dinitrobenzene on ψ -cumylhydrazine in boiling alcoholic solution. It is obtained as an orange-yellow, crystalline powder, which melts and decomposes at 154°. ψ -Cumeneazo-5-chloro-2-nitrobenzene, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NO}_2$, crystallises in orange-red needles and melts at 178°. ψ -Cumeneazoimino-

5-chlorobenzene oxide, $\text{C}_6\text{H}_3\text{Cl} \left\langle \begin{smallmatrix} \text{N}^- \\ | \\ \text{NO} \end{smallmatrix} \right\rangle \text{N} \cdot \text{C}_6\text{H}_2\text{Me}_3$, crystallises in yellow needles and melts at 137°. ψ -Cumeneazoiminochlorobenzene, $\text{C}_{15}\text{H}_{14}\text{N}_3\text{Cl}$, crystallises in slightly yellow needles and melts at 115°.

s-Acetyl- ψ -cumylhydrazide, $\text{C}_6\text{H}_2\text{Me}_3 \cdot \text{NH} \cdot \text{NHAc}$, formed by boiling ψ -cumylhydrazine with glacial acetic acid, crystallises in white leaflets and melts at 147°. s-Benzoyl- ψ -cumylhydrazide is colourless and melts at 164°.

G. Y.

p-Xylylhydrazine, and Picryl-, *o*-*p*-Dinitrophenyl-, and 5-Chloro-2-nitrophenyl-*p*-xylylhydrazines. CONRAD WILLGERODT and WILLY LINDENBERG (*J. pr. Chem.*, 1905, [ii], 71, 398—409).—*p*-Xylylhydrazine, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH} \cdot \text{NH}_2$, is formed by reduction of sodium *p*-xylenediazonium sulphite with zinc dust and acetic acid, decomposition of the product with hydrochloric acid, and liberation of the hydrazine by treatment with sodium hydroxide; it crystallises in glistening, white, slender needles, melts at 78°, and decomposes when exposed to air and light. The hydrochloride, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{HCl}$, crystallises in glistening, slender needles and melts at 212°; the platinichloride, $(\text{C}_8\text{H}_{12}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, forms a yellow powder; the sulphate, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{H}_2\text{SO}_4$, forms colourless crystals; the nitrate, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{HNO}_3$, crystallises in glistening scales. *p*-Xylylbenzylidenhydrazine forms yellow crystals and melts at 110°; benzophenone-*p*-xylylhydrazone forms a yellow, crystalline powder and melts at 103°.

s-Picryl-*p*-xylylhydrazine, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}_2\text{H}_2 \cdot \text{C}_6\text{H}_3\text{Me}_2$, formed by the

action of picryl chloride on *p*-xylylhydrazine in alcoholic solution, crystallises in small, red, slender needles, melts and decomposes at 169°, is stable when dry, and when boiled with glacial acetic acid in a reflux apparatus yields *p*-xyleneazoimino-4:6-dinitrobenzene oxide, $C_6H_2(NO_2)_2 \left\langle \begin{smallmatrix} N \\ | \\ NO \end{smallmatrix} \right\rangle N \cdot C_6H_3Me_2$, which crystallises in golden needles,

melts at 235°, and is soluble in most organic solvents. *p*-Xyleneazoiminodinitrobenzene, $C_6H_2(NO_2)_2 \left\langle \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} \right\rangle N \cdot C_6H_3Me_2$, is formed when picryl-*p*-xylylhydrazine is heated with alcohol in a sealed tube at 120° for 2—3 hours, or when *p*-xyleneazoiminodinitrobenzene oxide is boiled with 1 mol. of potassium iodide and a little water in glacial acetic acid solution in a reflux apparatus; it crystallises in yellow needles and melts at 125°. When boiled with 4 mols. of potassium iodide in glacial acetic acid for 2 days, *p*-xyleneazoiminodinitrobenzene oxide is reduced to a substance, $C_{14}H_{11}O_3N_5$, which crystallises in yellow needles and melts at 128°.

p-Xyleneazotrinitrobenzene, formed by oxidation of picryl-*p*-xylylhydrazine with chromic acid in glacial acetic acid solution, crystallises in brown needles and melts at 172°.

o-*p*-Dinitrophenyl-*p*-xylylhydrazine, $C_6H_3(NO_2)_2 \cdot N_2H_2 \cdot C_6H_3Me_2$, formed from *p*-xylylhydrazine and 1-chloro-2:4-dinitrobenzene, crystallises in small, slender needles and melts at 190°. *p*-Xyleneazoimino-*p*-nitrobenzene oxide forms yellow crystals and melts at 167°. *p*-Xyleneazoimino-*p*-nitrobenzene crystallises in yellow needles and melts at 158°.

p-Xyleneazoimino-*p*-aminobenzene, $NH_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} \right\rangle N \cdot C_6H_3Me_2$, forms a green, crystalline powder, melts at 195°, and forms fluorescent solutions; the *platinichloride*, $(C_{14}H_{14}N_4)_2, H_2PtCl_6$, forms a yellowish-red powder.

p-Xyleneazoiminobenzene is a white, flocculent substance, which melts at 136° and is volatile in a current of steam.

p-Xyleneazo-2:4-dinitrobenzene crystallises in glistening, red needles and melts at 157°.

5-Chloro-2-nitrophenyl-*p*-xylylhydrazine, $C_6H_3Me_2 \cdot N_2H_2 \cdot C_6H_3Cl \cdot NO_2$, formed from *p*-xylylhydrazine and 1-chloro-3:4-dinitrobenzene, crystallises in slender, red needles and melts at 144°. *p*-Xyleneazoimino-5-chlorobenzene oxide, $C_6H_3Cl \left\langle \begin{smallmatrix} N \\ | \\ NO \end{smallmatrix} \right\rangle N \cdot C_6H_3Me_2$, crystallises in yellow

leaflets, melts at 119°, and on reduction with potassium iodide and glacial acetic acid yields a dark oil. *p*-Xyleneazo-5-chloro-2-nitrobenzene, $C_6H_3Me_2 \cdot N_2 \cdot C_6H_3Cl \cdot NO_2$, forms small, red crystals and melts at 132°.

s-Acetyl-*p*-xylylhydrazide, $C_6H_3Me_2 \cdot NH \cdot NHAc$, forms white crystals and melts at 196°. *s*-Benzoyl-*p*-xylylhydrazide forms glistening, white crystals and melts at 181°.

G. Y.

p-Ethylphenylhydrazine, Picryl- and *o*-*p*-Dinitrophenyl-*p*-ethylphenylhydrazines and their Derivatives. CONRAD WILLGERODT and HANS HARTER (*J. pr. Chem.*, 1905, [ii], 71, 409—416).—*p*-Ethylphenylhydrazine, $C_6H_4Et \cdot N_2H_3$, is formed on reduction of sodium

p-ethylphenyldiazonium sulphite, treatment of the product with hydrochloric acid, and liberation of the hydrazine by means of dilute ammonia; it crystallises in glistening leaflets and is unstable even in the form of its salts. The *hydrochloride*, $C_8H_{12}N_2 \cdot HCl$, crystallises in white leaflets and melts at 200° ; the *platinichloride*, $(C_8H_{12}N_2)_2 \cdot H_2PtCl_6$, forms a red powder; the *sulphate*, $C_8H_{12}N_2 \cdot H_2SO_4$, crystallises in red leaflets and melts at 180° ; the *picrate*, $C_8H_{12}N_2 \cdot C_6H_3O_7N_3$, crystallises in yellow needles and melts at 122° . *p*-Ethylphenylbenzylidenehydrazine, $C_6H_4Et \cdot NH \cdot N : CHPh$, is obtained as a white, flocculent precipitate which melts at 78° . *p*-Ethylphenyltolylidenehydrazine, $C_{16}H_{18}N_2$, crystallises in yellow needles and melts at 175° .

Picryl-p-ethylphenylhydrazine, $C_6H_4Et \cdot NH \cdot NH \cdot C_6H_2(NO_2)_3$, crystallises in slender, red needles and melts at 145° . *p*-Ethylbenzeneazoismino-4:6-dinitrobenzene oxide, $C_6H_2(NO_2)_2 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NO \end{smallmatrix} \cdot C_6H_4Et$, crystallises in golden leaflets and decomposes at 200° . *p*-Ethylbenzeneazoismino-4:6-dinitrobenzene, $C_6H_2(NO_2)_2 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \cdot C_6H_4Et$, crystallises in yellow leaflets and melts at 140° . 2:4:6-Trinitrobenzeneazo-*p*-ethylbenzene $C_6H_2(NO_2)_3 \cdot N_2 \cdot C_6H_4Et$, crystallises in golden leaflets and melts at 192° .

o-p-Dinitrophenyl-*p*-ethylphenylhydrazine, $C_6H_3(NO_2)_2 \cdot N_2H_2 \cdot C_6H_4Et$, is obtained as an oil by mixing alcoholic solutions of *p*-ethylphenylhydrazine and 1-chloro-2:4-dinitrobenzene.

p-Ethylbenzeneazoismino-*p*-nitrobenzene, $NO_2 \cdot C_6H_3 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \cdot C_6H_4Et$, formed by boiling 2 mols. of *p*-ethylphenylhydrazine with 1 mol. of 1-chloro-2:4-dinitrobenzene in alcoholic solution, crystallises in red leaflets and melts at 125° . *p*-Ethylbenzeneazoismino-*p*-aminobenzene, $NH_2 \cdot C_6H_3 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ N \end{smallmatrix} \cdot C_6H_4Et$, crystallises in slender, red or yellow needles, melts at 155° , and forms fluorescent solutions; the *platinichloride*, $(C_{14}H_{14}N_3)_2 \cdot H_2PtCl_6$, forms a yellow powder. G. Y.

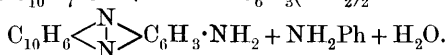
Yellow Sulphur Dye from Nitro-*o*-methylbenziminazole. CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 157862).—

Nitro-*o*-methylbenziminazole, $NO_2 \cdot C_6H_3 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} \cdot CMe$, best prepared by boiling nitro-*o*-phenylenediamine with glacial acetic acid (compare Heim, Abstr., 1888, 1097), does not yield a dye when heated alone with sulphur, but a mixture of the nitro- or amino-compound with benzidine, when fused with sulphur and sodium sulphide, yields a yellow dye of slightly greenish shade. C. H. D.

Naphthaphenazines. AKT. - GES. FÜR ANILIN - FABRIKATION (D.R.-P. 157861).—*o*-Aminoazo-compounds react with β -naphthol when fused together at 205 — 215° , forming naphthaphenazines. Thus β -naphthol and chrysoidine yield Nietzki's 8-aminonaphthaphenazine (Abstr., 1888, 843), thus: $C_{10}H_7 \cdot OH + NPh \cdot N \cdot C_6H_3(NH_2)_2 = NH_2Ph +$

$\text{H}_2\text{O} + \text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NH}_2$. In similar manner, *o*-aminoazotoluene yields naphthato-luazine. C. H. D.

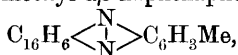
New Naphthazine Syntheses from *o*-Aminoazo-compounds. FRITZ ULLMANN and J. S. ANKERSMIT (*Ber.*, 1905, 38, 1811—1822).—Naphthazines may be obtained with a good yield by fusing *o*-aminoazo-compounds with substituted naphthols; thus in the case of chrysoidine and β -naphthol, 8-amino- $\alpha\beta$ -naphthaphenazine is obtained according to the equation $\text{C}_{10}\text{H}_7 \cdot \text{OH} + \text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{NH}_2)_2 =$



8-Aminonaphthaphenazine hydrochloride crystallises from dilute acetic acid in red leaflets with a bronze lustre and melts and decomposes at 264° ; the *nitrate* forms similarly coloured needles and melts and decomposes at 243° . The *methochloride*, $\text{C}_{17}\text{H}_{14}\text{N}_3\text{Cl}$, forms small, red needles with a green reflex and melts at 264° . 8-Acetaminonaphthaphenazine crystallises from aniline in yellow needles and melts at 298° .

8-Amino-9-methyl- $\alpha\beta$ -naphthaphenazine, $\text{C}_{10}\text{H}_8 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_2\text{Me} \cdot \text{NH}_2$, prepared from β -naphthol and 5-benzeneazotolyene-2:4-diamine, crystallises from xylene in bright yellow, concentric aggregates of needles and melts at 249° ; the *sulphate* forms small, red, felted needles, the *hydrochloride* melts and decomposes at 283° , and the *acetyl* derivative, $\text{C}_{19}\text{H}_{14}\text{ON}_3$, crystallises from nitrobenzene in yellow needles and melts at 295° .

9-Tolunaphthazine [9-methyl- $\alpha\beta$ -naphthaphenazine],

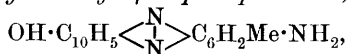


prepared from *o*-aminoazotoluene and β -naphthol, is identical with Witt's product (*Abstr.*, 1887, 591). Benzeneazo- β -naphthylamine and β -naphthol combine together on fusion to form *s*- $\alpha\beta$ -naphthazine (Matthes, *Abstr.*, 1890, 992).

8-Amino-2-hydroxynaphthaphenazine, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NH}_2$,

prepared from chrysoidine and 2:7-dihydroxynaphthalene, crystallises from aniline or nitrobenzene in small, yellowish-brown needles and melts at 350° .

8-Amino-2-hydroxy-9-methyl- $\alpha\beta$ -naphthaphenazine,



prepared from 5-benzeneazotolyene-2:4-diamine and 2:7-dihydroxynaphthalene, crystallises from aniline in yellowish-brown needles and does not melt at 360° ; the *hydrochloride* forms red needles with a bronze-like lustre.

2-Hydroxy-*s*- $\alpha\beta$ -naphthazine, $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_{10}\text{H}_5 \cdot \text{OH}$, prepared from benzeneazo- β -naphthylamine and 2:7-dihydroxynaphthalene, crystallises from aniline in greenish-yellow needles and melts at 301° .

On heating benzeneazo-*m*-tolylenediamine with 2:3-dihydroxynaphthalene at 150—160°, a mixture of 8-*amino*-6-*hydroxy*-9-*methyl*- $\alpha\beta$ -*naphthaphenazine*, $C_{17}H_{13}ON_3$, and 8-*amino*-6-*anilino*-9-*methyl*- $\alpha\beta$ -*naphthaphenazine*, $NHPh \cdot C_{10}H_5 \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > C_6H_2Me \cdot NH_2$, is obtained. The former crystallises from aniline in yellowish-brown needles, melts at 254°, and gives a *sodium* salt which crystallises in yellow needles; the latter crystallises from aniline in lustrous, reddish-brown needles and melts at 270·5°.

8-*Amino*-6-*hydroxynaphthaphenazine*, $C_{16}H_{11}ON_3$, prepared from chrysoidine and 2:3-dihydroxynaphthalene, forms reddish-brown needles and melts at 263°. W. A. D.

Trihydroxyphenylosinduline. KALLE & Co. (D.R.-P. 158077 and 158100).—A trihydroxyphenylosinduline is obtained when *p*-aminophenol is fused at 160—170° with benzeneazo- α -naphthylamine, 1:4-naphthylenediamine, or α -naphthylamine. In the last two cases, the presence of an oxidising agent, such as *p*-nitrophenol or α -nitronaphthalene, is necessary. The product is insoluble in water, benzene, or dilute acids, but dissolves in alcohol or dilute alkali hydroxides to bluish-violet solutions. If *m*-nitroaniline or *p*-nitroaniline is employed as the oxidising agent, an equivalent quantity of *p*-aminophenol is saved, and the yield of rosinduline is improved. C. H. D.

Electrolytic Reduction of the Nitrocinnamic Acids. CHARLES MARIE (*Compt. rend.*, 1905, 140, 1248—1250).—When *m*- and *p*-nitrocinnamic acids are reduced in alkaline solution at a platinum cathode with a current density of 5 amperes per sq. dm., the corresponding azoxy-acids are obtained in 80 per cent. yield; hydrogen is not evolved until the reaction is practically complete. The azoxycinnamic acids are yellow and insoluble in water and in most of the ordinary solvents, but dissolve to some extent in boiling acetic acid and boiling pyridine. The *m*-acid melts at 335—337°; the *p*-acid decomposes at 360° without melting. Both acids dissolve in warm concentrated sulphuric acid to intense orange-red solutions. The solution of the *m*-acid when heated at 150—160° turns brown, and on dilution and neutralisation a *substance* separates in yellow plates, which melts at 162° and dissolves in water, alcohol, or benzene. The *sodium* salts of the azoxycinnamic acids are only slightly soluble in water. The *silver* salts are faintly coloured, and the *methyl* and *ethyl* esters crystallise from amyl alcohol in brilliant orange needles.

m-Aminocinnamic acid is a secondary product in the reduction of *m*-nitrocinnamic acid, but practically no *m*-aminohydrocinnamic acid is formed. On the other hand, *p*-aminohydrocinnamic acid is the only secondary product in the reduction of *p*-nitrocinnamic acid. When the quantity of electricity passed through the solution is smaller than that theoretically required for the production of the azoxy-acid, small quantities of *p*-nitrohydrocinnamic acid melting at 161° are obtained. Electrolytic reduction of *p*-aminocinnamic acid at a mercury cathode affords the most convenient method of obtaining the corresponding hydro-acid.

o-Nitrocinnamic acid does not yield an azoxy-acid on electrolytic reduction.
H. M. D.

Conversion of Diazoamino-*p*- into Aminoazo-*p*-toluene in the Solid State. COENRAAD L. JUNGUS (*Chem. Centr.*, 1905, i, 1464—1465; from *Chem. Weekblad*, 2, 246—249).—The velocity with which the change of diazoamino-*p*-toluene into aminoazo-*p*-toluene takes place at the ordinary temperature has been followed during a period of 1½ years. Mixtures were made by melting together 25 grams of *p*-toluidine (m. p. 45°) with 2·812 grams of diazoamino-*p*-toluene and quantities of *p*-toluidine hydrochloride varying from about 0·7—2·9 grams and quickly cooling the mass. The quantity of nitrogen which was evolved when the mass was treated with dilute sulphuric acid was determined from time to time. Pure diazoamino-*p*-toluene (m. p. 116°) was found to change more slowly than less pure preparations. The extremely small initial velocity increases rapidly, the *p*-toluidine hydrochloride possibly acting as a catalytic agent. The change is distinctly apparent, however, when the hydrochloride is not present, but as the quantity of this salt is increased, the velocity also increases, although not proportionately. Aminoazo-*p*-toluene can also be detected when the substances are merely mixed together and not melted. The maximum change was observed in the case of a mixture obtained by melting together 25 grams of toluidine with 2·812 grams of diazoamino-*p*-toluene and 2·870 grams of toluidine hydrochloride, 94 per cent. being converted into the aminoazo-compound in 13 months.
E. W. W.

Carbohydrates from Serum Globulins. III. LEO LANGSTEIN (*Monatsh.*, 1905, 26, 531—535. Compare Abstr., 1903, i, 734; 1904, i, 790).—Serum globulin, which had been washed with hot water for 4 weeks, dried, and extracted with alcohol, yielded dextrose when treated with 3 per cent. hydrochloric acid. This dextrose is probably in glucoside combination with the albumin. Lævulose is now found not to be present in serum globulin. The total carbohydrates obtained from serum globulin amount to about 1 per cent., of which about 1/3 is dextrose.

Contrary to Abderhalden, Bergell, and Dörpinghaus' statement (Abstr., 1904, i, 640), serum globulin contains glucosamine, which is separated as the hydrochloride from the benzoic esters obtained as previously described. A small amount of a hydroxyamino-acid was obtained by the trypsin digestion of the syrup formed by the action of an aqueous alkali hydroxide on serum globulin, and precipitation with alcohol.
G. Y.

Precipitation Limits with Ammonium Sulphate of some Vegetable Proteids. THOMAS B. OSBORNE and ISAAC F. HARRIS (*Amer. J. Physiol.*, 1905, 13, 436—447. Compare Abstr., 1903, i, 871).—Hofmeister's method of fractional precipitation with ammonium sulphate is regarded as a valuable and ready means of separating proteids in solution. The precipitation limits are not characteristic for each proteid, but depend on the conditions existing in the solution at the time of precipitation. In several experiments, the two products ob-

tained, the one by precipitating a large part of the dissolved proteid at a definite degree of saturation, and the other obtained from its filtrate at one-tenth higher saturation, after separation from solution by dialysis were found to have the same limits of precipitation as one another, which limits were lower and wider apart than those between which the separation was first made. The products were also alike in composition and properties.

Vegetable globulins and albumins cannot be separated by means of their precipitation limits with ammonium sulphate; some globulins require more than half saturation and some albumins (such as leucosin) less for precipitation.

W. D. H.

Hæmatogen. HUGOUNENQ and MOREL (*Compt. rend.*, 1905, 140, 1065—1067).—The analyses of hæmatogen given by Miescher and Bunge are not concordant. The percentage composition found in the present research was: C, 43·5; H, 6·9; N, 12·6; P, 8·7; Fe, 0·455; Ca, 0·352; Mg, 0·126; S, traces; O, 27·367. The numbers differ a little from those of Bunge, and are attributed to the material having been freed from all traces of fat and albumin.

W. D. H.

Fractional Hydrolysis of Optically Active Esters by Lipase. II. HENRY D. DAKIN (*J. Physiol.*, 1905, 32, 199—206. Compare Abstr., 1904, i, 1071).—The partial hydrolysis of the inactive esters of mandelic acid and its alkyl derivatives results in the production of a dextrorotatory free acid and a lævorotatory residue of unchanged ester. In those derivatives in which hydroxyl is replaced by a halogen atom, a lævorotatory free acid and a dextrorotatory residue of ester are the resulting products. When a series of allied, optically inactive esters is hydrolysed by lipase, the active components which are most readily attacked have a similar molecular configuration, but not necessarily the same sign of rotation. The partial hydrolysis of an optically inactive ester in which the asymmetric carbon atom is situated in the alkyl instead of the acyl group, as in the other esters examined, also yields optically active products, showing that the enzyme presumably combines with the molecule as a whole.

W. D. H.

Preparation of Pepsin. P. SCHRUMPF (*Beitr. chem. Physiol. Path.*, 1905, 6, 396—397).—The mucous membrane from pig's stomach was subjected to pressure, as in Buchner's work on yeast, and the liquid filtered through a Chamberland filter. Pepsin was separated from the filtrate by the cholesterol method. The pepsin solution was proteid-free. In some cases the solution had rennetic properties, in other cases not, a fact which tells against the view of Pawloff and Nencki that pepsin and rennin action are both due to the same molecule.

W. D. H.

Organic Chemistry.

Some Reactions of Acetylene. JULIUS A. NIEUWLAND (*Chem. Centr.*, 1905, i, 1585—1586; from *J. Gasbel.*, 48, 387—388).—When acetylene is reduced electrolytically, using a cathode of calcium carbide, only a minute quantity of ethylene is liberated; the formation of alcohol observed by Billitzer has not been confirmed. In the presence of sulphuric acid, however, acetaldehyde is formed. The platinum possibly acts in the latter case as a catalytic agent, for the aldehyde is also obtained when acetylene is passed through water containing platinum sponge and a small quantity of nitric acid.

Experiments have shown that the explosions which occur when acetylene is treated with chlorine cannot be ascribed solely to the presence of oxygen (compare Mouneyrat, *Abstr.*, 1898, i, 613). Chlorine hydrate does not cause explosions when brought in contact with acetylene or calcium carbide in open vessels, but in closed vessels explosions occur, carbon and hexachloroethane being formed. When chlorine is passed into a solution of acetylene in acetone or acetylene into a solution of chlorine in carbon tetrachloride at 0°, slight explosions take place where the gases mix above the liquid. If the solution of one gas is gradually added below the surface of the solution of the other, the heat of the reaction causes the gases to escape and a cloud of soot containing hexachloroethane is formed, whilst chloroacetone remains in solution. Tetrachloroacetylene is formed by the direct action of the gases at 1—2°; when an appreciable excess of chlorine is used, the gas burns with a small flame at the end of the delivery tube, and hexachloroethane and carbon are formed. Explosions are invariably accompanied by the formation of hexachloroethane: $2C_2H_2 + 5Cl_2 = C_2Cl_6 + 4HCl + 2C$. The energy liberated by this decomposition is sufficient to cause explosion of the rest of the mixture, the reaction $C_2H_2 + Cl_2 = 2HCl + 2C$ taking place. This hypothesis is supported by the fact that when a very rapid stream of acetylene is passed into bromine water cooled by ice, the gas takes fire, although bromine is much less active than chlorine; ethylene also explodes with chlorine under certain conditions.

When chlorine and acetylene are passed into a flask containing boiling water, tetrachloroacetylene is formed without explosion, and at 140° the gases also react quietly, forming tetrachloroacetylene and hexachloroethane; at 270°, the gases, when diluted with hydrogen chloride, also form the same products without explosion. The action of chlorine compounds on acetylene has also been investigated. The experiments have an important bearing on the explosions which sometimes occur in the process of purifying acetylene by means of bleaching powder.

E. W. W.

A Simple Method for the Formation and Preparation of Alkyl Haloids. RUDOLF F. WEINLAND and KARL SCHMID (*Ber.*, 1905, 38, 2327).—Methyl sulphate (or ethyl sulphate) readily reacts in

aqueous solution with potassium iodide, thus: $\text{Me}_2\text{SO}_4 + \text{KI} = \text{MeI} + \text{KMeSO}_4$. Methyl chloride may be prepared by heating a mixture of potassium methyl sulphate with potassium chloride; when potassium bromide is used in place of potassium chloride, methyl bromide is formed together with other products, whilst, when potassium iodide is used, iodine is evolved.

A. McK.

Constitution of Hexyl Iodide from Mannitol. P. RASETTI (*Bull. Soc. chim.*, 1905, [iii], 33, 691—693).—When the hexyl iodide obtained by Hecht's method (this Journal, 1873, 370) from mannitol is treated with potassium cyanide dissolved in alcohol, the mixture of nitriles formed is a colourless, mobile liquid, which boils at 166—168° under atmospheric or at 72° under 27 mm. pressure. The mixture of hexylformamides, obtained by treating the mixed nitriles with sodium hydroxide in alcohol, forms silky needles, and by fractional crystallisation from warm carbon disulphide is separated into α -ethylvaleramide and α -methylhexoamide (compare this vol., i, 561, 562). The hexyl iodide obtained from mannitol is therefore a mixture of the β - and γ -iodohexanes (compare Wanklyn and Erlenmeyer, this Journal, 1863, 223, and Combes and Le Bel, *Abstr.*, 1893, i, 246).

T. A. H.

aci-Dinitro-alcohols. I. PAUL DUDEN and G. PONNDORF (*Ber.*, 1905, 38, 2031—2036).—Aldol formation takes place when aliphatic aldehydes interact with the alkali salts of *aci*-dinitromethane, thus: $\text{R}\cdot\text{CHO} + \text{NO}_2\cdot\text{CH}\cdot\text{NO}_2\text{K} = \text{R}\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{NO}_2)_2\cdot\text{NO}_2\text{K}$.

Potassium aci-dinitroethyl alcohol, $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)_2\cdot\text{NO}_2\text{K}$, prepared by the action of formaldehyde on potassium *aci*-dinitromethane, crystallises in rhombic plates. Formaldehyde is evolved when its aqueous solution is boiled. The free *acid* is an oil easily soluble in water; when its aqueous solution is boiled, a vigorous evolution of nitric oxide and carbon dioxide occurs, and a *compound*, $\text{C}_5\text{H}_2\text{O}_7\text{N}_4$, is formed which crystallises in glistening leaflets and melts and decomposes at 190°.

Potassium aci-dinitroisopropyl alcohol, $\text{OH}\cdot\text{CHMe}\cdot\text{C}(\text{NO}_2)_2\cdot\text{NO}_2\text{K}$, prepared by the action of an excess of acetaldehyde on potassium *aci*-dinitromethane, forms lemon-yellow crystals. The free *acid* is an oil having the sp. gr. 1.33 at 15°/4° and n_D 1.449 at 15°; its aqueous solution decomposes when boiled.

sec-aci-Dinitrobutyl alcohol, $\text{C}_4\text{H}_8\text{O}_5\text{N}_2$, is an oil which is sparingly soluble in water; its *potassium* salt forms yellow, glistening leaflets and explodes at 205°.

sec-aci-Dinitroamyl alcohol (*aci-dinitromethylpropylcarbinol*), $\text{C}_5\text{H}_{10}\text{O}_5\text{N}_2$,

is a colourless oil; its *potassium* salt forms glistening, yellow leaflets. The dissociation of the latter was examined quantitatively.

A. McK.

Derivatives of *aaa*-Trichloroisopropyl Alcohol. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1905, 101—121. Compare *Abstr.*, 1904, i, 279, 794, and this vol., i, 110).—When *aaa*-trichloroisopropyl alcohol

dissolved in light petroleum is treated with phosphorus trichloride there are formed (1) trichloropropylene, $\text{CCl}_3\cdot\text{CH}:\text{CH}_2$ (this vol., i, 110); (2) *trichloroisopropyl dichlorophosphite*, $\text{PCl}_2\cdot\text{O}\cdot\text{CHMe}\cdot\text{CCl}_3$; (3) *trichloroisopropyl chlorophosphite*, $\text{PCl}[\text{O}\cdot\text{CHMe}\cdot\text{CCl}_3]_2$ (a thick liquid, which boils at 210° under 25 mm. pressure, and in contact with water regenerates trichloroisopropyl alcohol), and (4) *trichloroisopropylphosphite*, $\text{P}[\text{O}\cdot\text{CHMe}\cdot\text{CCl}_3]_3$. The formation of the three esters in this reaction indicates that Jaroschenko's rule that the corresponding olefinic hydrocarbon is the principal product of the action of phosphorus trichloride on *sec.*-alcohols (*Chem. Centr.*, 1897, ii, 334) is not generally applicable. Trichloroisopropyl dichlorophosphite is a colourless, rather thick liquid, which boils at $223\text{--}224^\circ$ under 758 mm. pressure and at 140° under 70 mm. pressure, has a sp. gr. 1.5870 at 20° , and reacts with chlorine to form *aaa-trichloroisopropyl chloride*, $\text{CCl}_3\cdot\text{CHMeCl}$. This is a colourless, limpid liquid, which boils at $152\text{--}153^\circ$, has a sp. gr. 1.473 at 20° and n_D 1.4867. The corresponding *bromide*, similarly prepared, boils at $171\text{--}172^\circ$ under 766 mm. pressure and has a sp. gr. 1.775 at 20° .

When *aaa-trichloroisopropyl alcohol* is treated with phosphorus pentachloride, trichloropropylene is formed in small amount, and the principal product is a *trichloroisopropyl chlorophosphate* having the constitution $\text{POCl}[\text{O}\cdot\text{CHMe}\cdot\text{CCl}_3]_2$. This is a viscous liquid, which dissolves in ether and from such solutions separates as a crystalline *additive product*, which reverts to the original substance when dried by exposure over sulphuric acid. It is decomposed by water, forming a *phosphate* of the constitution $\text{HO}\cdot\text{PO}[\text{O}\cdot\text{CHMe}\cdot\text{CCl}_3]_2$, which is at first viscous and eventually becomes a crystalline magma.

s-Hexachloroisopropyl formal, $\text{CH}_2[\text{O}\cdot\text{CHMe}\cdot\text{CCl}_3]_2$, obtained by the interaction of *aaa-trichloroisopropyl alcohol* with trioxymethylene in presence of zinc chloride (compare Stappers, this vol., i, 261), is a colourless, viscous liquid, possessing a strong odour and bitter taste. It boils at 290° under 750 mm. pressure, does not solidify at -80° , has a sp. gr. 1.481 at 20° , and is insoluble in water. T. A. H.

Presence of Acetylmethylcarbinol in certain Commercial Vinegars. PASTUREAU (*J. Pharm. Chim.*, 1905, [vi], 21, 593—595).—A sample of vinegar, which gave an abundant precipitate when treated with alcohol and reduced Fehling's solution in the cold, was found to contain about 0.3 per cent. of acetylmethylcarbinol. The latter was identified by the melting point (243°) of its osazone and estimated by its silver reducing power. Its presence in the vinegar was probably due to the action of bacteria of the *tartricus* species on the carbohydrates. W. P. S.

Action of Dilute Sulphuric Acid on the Glycol obtained by Reduction of Propionaldol. JULIUS MUNK (*Monatsh.*, 1905, 26, 663—674. Compare Thalberg, *Abstr.*, 1898, i, 550).—The glycol, $\text{C}_6\text{H}_{14}\text{O}_2$, boils at $100\text{--}102^\circ$ under 14 mm. or at 214° under ordinary pressure, and, when heated with 20 per cent. sulphuric acid at 100° in a sealed tube, yields principally the dioxide, $\text{C}_{12}\text{H}_{24}\text{O}_2$, along with small quantities of an unsaturated hydrocarbon and a ketone.

The hydrocarbon, C_6H_{10} , is a colourless, mobile oil with an odour of terpin, which boils at 69° under the ordinary pressure, and forms an additive compound with 1 mol. of bromine.

The ketone, $COEtPr^{\beta}$, boils at 114° and forms an *oxime*, $C_6H_{13}ON$, which is a colourless, mobile liquid boiling at 74° under 11 mm. pressure. When boiled with acetic anhydride, the oxime forms the *acetyl* derivative, $C_6H_{12}ONAc$, which is a transparent, mobile liquid with an ester-like odour and boils at $94-96^\circ$ under 14 mm. pressure. As the ketone reduces ammoniacal silver solution, it probably contains traces of methylisopropylacetaldehyde, which boils at 116° .

The *dioxide*, $O \left\langle \begin{array}{c} CHEt \cdot CHMe \cdot CH_2 \\ CH_2 \cdot CHMe \cdot CHEt \end{array} \right\rangle O$, is a yellow, mobile oil, which boils at 102° under 13 mm. or at 214° under the ordinary pressure, is insoluble in water, and does not enter into reaction with zinc ethyl at 100° or with water at 200° .
G. Y.

Action of Silver Cyanate on Acyl Chlorides. IV. Methanesulphonylcarbimide. OTTO C. BILLETER (*Ber.*, 1905, 38, 2013—2015. Compare Abstr., 1903, i, 821; 1904, i, 397).—When molecular amounts of silver cyanate and methanesulphonic chloride are heated at 120° , a violent action occurs with the formation of a yellow product, which does not contain cyanate and which is probably methanesulphonic anhydride. When the action was moderated, the presence of methanesulphonic anhydride (compare this vol., i, 584) in the reaction mixture was detected. The portion of the latter which distilled at $50-80^\circ$ under 10 mm. pressure was again treated with silver cyanate, the lower boiling fraction again separated, and the treatment with silver cyanate repeated in this manner eight times, when *methanesulphonylcarbimide*, $CH_3 \cdot SO_2 \cdot N \cdot CO$, was isolated. It melts at 31° , boils at $73.5-75^\circ$ under 10 mm. pressure, solidifies in rhombic plates, and separates from ether in needles. It is very readily attacked by water and by alcohol. With water, it forms methanesulphonamide.
A. MCK.

Action of Sodium on Aliphatic Esters. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1905, 140, 1593—1595. Compare Abstr., 1903, i, 597, 673; 1904, i, 642, 730).—The dry aliphatic ester is added slowly and in small quantities at a time to sodium wire suspended in dry ether contained in a flask cooled by immersion in ice. When the whole of the ester has been added, the flask is withdrawn from the ice and allowed to assume the atmospheric temperature; it is then set aside until the whole of the sodium has been converted into a white or bright yellow powder.

Applying this process to ethyl butyrate, there are produced (1) butyrolin, $COPr^a \cdot CHPr^a \cdot OH$, which boils at 95° under 20 mm. pressure, has a sp. gr. 0.9367 at $0^\circ/4^\circ$, and is identical with that obtained by Klinger and Schmitz (Abstr., 1891, 890); (2) dibutyryl; and (3) a *substance*, produced by the condensation of 2 mols. of butyrolin with the loss of a mol. of water. This is a liquid which boils at $155-157^\circ$ under 12 mm. pressure and has a sp. gr. 0.9398 at $0^\circ/4^\circ$.

Under the same conditions, ethyl hexoate yields *caproin*, $C_{12}H_{24}O_2$, a

liquid boiling at 142° under 10 mm. pressure, *dihexoyl*, which boils at 120° under 10 mm. pressure and furnishes a *dioxime* melting at 181° , and *dicaproin*, produced by the condensation of 2 mols. of caproin with the loss of a mol. of water, which boils at $215\text{--}220^{\circ}$ under 10 mm. pressure.

It appears that this reaction may furnish a general method of preparing α -disecundary glycols and s - α -diketones (compare this vol., i, 572).
T. A. H.

Derivatives of Normal Hexoic Acid. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1905, 158—177).—*n*-Hexonitrile, prepared by dehydrating the corresponding amide with phosphoric oxide, is a colourless, pleasant-smelling liquid with a sweetish taste; it boils at $162\text{--}163^{\circ}$ under 750 mm. pressure, has a sp. gr. 0.8093 at 20° and n_D 1.41154. *iso*Hexonitrile boils at $154\text{--}155^{\circ}$.

n-Hexyl chloride, prepared from hexyl alcohol obtained from hexoic acid by Bouveault and Blanc's process (*Abstr.*, 1904, i, 642), boils at $134\text{--}135^{\circ}$ under 763 mm. pressure, has a sp. gr. 0.8720 at 20° and n_D 1.4244.

n-Hexyl mercaptan, obtained by treating hexyl iodide with potassium hydrogen sulphide in alcohol, boils at $149\text{--}150^{\circ}$ under 768 mm. pressure and has a sp. gr. 0.8486 at 20° . The substance described under this name by Pelouze and Cahours (*Compt. rend.*, 1862, 54, 1241) is probably the *sec*-hexyl mercaptan (compare Erlenmeyer and Wanklyn, *Trans.*, 1864, 17, 193). *n*-Amyl mercaptan boils at $126\text{--}127^{\circ}$.

n-Hexyl nitrite is a mobile, faintly yellow liquid with a pleasant odour; it boils at $129\text{--}130^{\circ}$ under 774 mm. pressure, has a sp. gr. 0.8851 at 20° and n_D 1.40181. With methyl alcohol, it yields methyl nitrite and hexyl alcohol. *n*-Nitrohexane, obtained by the action of silver nitrite on hexyl iodide, is a colourless liquid with a faint odour and sweetish taste; it boils at $193\text{--}194^{\circ}$ under 765 mm. or at 112° under 75 mm. pressure, and has a sp. gr. 0.9488 at 20° . The substances described under this name by Worstall (*Abstr.*, 1899, i, 399) and Auger (*Abstr.*, 1900, i, 578) are regarded as mixtures of normal nitro-hexane with *sec*-nitrohexane (Konowaloff, *Abstr.*, 1892, i, 575) and hexyl nitrite respectively.

n-Heptonitrile, obtained by the action of potassium cyanide on hexyl iodide dissolved in alcohol, boils at $183\text{--}184^{\circ}$ under 765 mm. pressure, has a sp. gr. 0.8153 at 20° and n_D 1.4195 (compare Mehlig, *Abstr.*, 1878, 134; and Hell and Kitrosky, *Abstr.*, 1891, 812).

The boiling points of the normal aliphatic nitriles and the corresponding alcohols are tabulated in the original and show that the change in boiling point due to the replacement of $-\text{CN}$ by $-\text{CH}_2\cdot\text{OH}$ in this series ranges from -1° to -8° except in the case of hydrocyanic acid and methyl alcohol where the change is $+40^{\circ}$.

T. A. H.

Methylbutylacetic [α -Methylhexoic] Acid. P. RASSETTI (*Bull. Soc. chim.*, 1905, [iii], 33, 687—691. Compare following abstract).—*Ethyl methylbutylmalonate*, $\text{C}_4\text{H}_9\cdot\text{CMe}(\text{CO}_2\text{Et})_2$, obtained by the action of normal butyl iodide on the sodium derivative of ethyl

malonate, boils at 235.5—237.5°. The *methyl ester* boils at 219—221°. The *free acid* crystallises in slender needles, melts at 99—101°, and yields crystalline *copper* and *barium* salts.

α -Methylhexoic acid, $C_4H_9 \cdot CHMe \cdot CO_2H$, obtained by heating the foregoing acid at 180°, boils at 209.5—211° (compare Kiliani, Abstr., 1886, 438, 441). The *methyl ester* boils at 159—160°, and the *ethyl ester* at 174—175°. α -Methylhexoamide separates in small needles from water or spangles from carbon disulphide and melts at 70—72.5°. The *chloride* of the acid and the calcium salt were also prepared (compare Kiliani, *loc. cit.*). T. A. H.

Ethylpropylacetic [α -Ethylvaleric] Acid. P. RASSETTI (*Bull. Soc. chim.*, 1905, [iii], 33, 684—687).—Ethyl ethylpropylmalonate, $CEtPr^a(CO_2Et)_2$, prepared by the action of ethyl bromide or iodide on the sodium derivative of ethyl propylmalonate, is a colourless oily liquid and boils at 234—236°. The *methyl ester* is similar, boils at 215—217°, has a sp. gr. 1.0335 at 0°/0° and 1.0140 at 21°/21° and n_D 1.43035 at 21°. The *acid* forms slender needles and melts at 117—118°. The *barium* and *copper* salts were prepared.

α -Ethylvaleric acid, $CH_3EtPr^a \cdot CO_2H$, prepared by heating ethylpropylmalonic acid at 180°, boils at 208—209° (compare Kiliani, Abstr., 1886, 441). The *methyl ester* boils at 155—156.5°, the *ethyl ester* at 169—171°, and the *chloride* at 158—160°. α -Ethylvaleramide crystallises from carbon disulphide and melts at 102.5—103.5°.

T. A. H.

Synthesis of Fats. AD. GRÜN (*Ber.*, 1905, 38, 2284—2287).— $\alpha\gamma$ -Diglycerides are formed by dissolving glycerol in sulphuric acid, and warming the disulphate so obtained with the fatty acid dissolved in concentrated sulphuric acid. $\beta\gamma$ -Diglycerides are formed in the same manner from glycerol α -chlorohydrin. The following glycerides have been prepared by this method.

$\alpha\gamma$ -Dipalmitin melts at 70°, and, when treated with an excess of acetic anhydride in pyridine solution, forms β -acetyl- $\alpha\gamma$ -dipalmitin, $OAc \cdot C_3H_5(O \cdot C_{16}H_{31}O)_2$, which separates from alcohol in spherical, crystalline aggregates, and melts at 49°, or after fusion and resolidification at 33°.

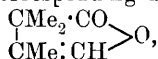
$\alpha\gamma$ -Distearin crystallises in white needles, sinters at 58°, and melts at 76° (m. p. 58°, Berthelot, this Journ., 1853, 6, 283; 76.5°, Hundeshagen, Abstr., 1884, 280). $\alpha\gamma$ -Diarachin melts at 75°.

Dipalmito- α -chlorohydrin, $C_3H_5Cl(O \cdot C_{16}H_{31}O)_2$, separates from alcohol as an oil which solidifies to small, soft crystals; it melts at 48—50°, yields potassium chloride on hydrolysis with alcoholic potassium hydroxide, and when heated with silver acetate and glacial acetic acid in a sealed tube at 140°, yields α -acetyl- $\beta\gamma$ -dipalmitin, which sinters at 52° and melts at 67°. A mixture of the α - and β -acetyl-dipalmitins commenced to melt at 49—50° and was clear at 63°.

G. Y.

Aldehydo-acids. EDMOND E. BLAISE and A. COURTOT (*Compt. rend.*, 1905, 141, 41—42. Compare Perkin and Sprankling, *Trans.*, 1899, 75, 11).— $\alpha\alpha\beta$ -Trimethyl- Δ^8 -butenoic acid, $CH_3 \cdot CMe \cdot CMe_2 \cdot CO_2H$

(m. p. 35°), when brominated, yields $\alpha\alpha\beta$ -trimethyl- $\beta\gamma$ -dibromobutyric acid (m. p. 125°), and this, when heated, furnishes a bromo-lactone, $\text{CMe}_2\text{—CO} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{O}$, which, in turn, by further heating, either alone or with quinoline, yields the corresponding unsaturated lactone,



and this, on hydrolysis, gave the corresponding aldehydo-acid, which, however, reacts as if it had the constitution $\text{CMe}_2\text{—CO} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{O} ; \text{OH·CH·CHMe}$;

this melts at 63° , has the mol. volume 130·47 in toluene (the open chain formula requires 146·1), reacts with phenylcarbimide, forming a phenylurethane melting at 134° , furnishes an acetyl derivative, and does not give Schiff's reaction or form acetals. On the other hand, the closed chain appears to be easily opened, since the characteristic aldehyde reactions with phenylhydrazine, hydroxylamine, &c., take place.

By a similar series of reactions, β -phenyl- $\alpha\alpha$ -dimethylbutyrolactone, having the constitution $\text{CHPh} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CMe}_2\text{·CO} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{O}$ and melting at 131° , was prepared.

T. A. H.

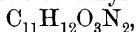
Ethyl Formylacetate and Ethyl α -Formylpropionate. ARTHUR MICHAEL (*Ber.*, 1905, **38**, 2096—2105. Compare this vol., i, 195).—Resorcinol and ethyl sodio- α -formylpropionate in absolute alcoholic solution form an additive compound, as in this the sodium is more fully neutralised than in ethyl sodio- α -formylpropionate. On expulsion of the alcohol and acidification of the reaction mixture, after three days, α -methylumbelliferone, $\text{OH·C}_6\text{H}_3 \begin{array}{c} \diagup \\ \diagdown \end{array} \text{O—CO} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH·CMe}_2$, is obtained as a gummy precipitate, which, on crystallisation from alcohol, forms white, prismatic needles, melts at $217\text{—}219^{\circ}$, and dissolves in aqueous alkali hydroxides to blue fluorescent solutions, from which it is precipitated unchanged on acidification.

The action of methyl iodide on ethyl sodioformylacetate in absolute alcoholic solution leads to the formation of ethyl trimesate and a small quantity of a neutral oil which boils at $69\cdot5\text{—}70\cdot5^{\circ}$ under 22 mm. pressure, and is possibly a mixture of the unchanged ester and its methyl derivative, or may be derived from an impurity in the sodio-ester (see Wislicenus and Bindemann, *Abstr.*, 1901, i, 361).

Ethyl α -formylpropionate is best formed by adding a mixture of ethyl formate and propionate to sodium under ether cooled by ice-water. After acidification and fractionation, a small, crystalline residue is obtained, which crystallises in silky leaflets and melts at $96\text{—}97^{\circ}$. The action of methyl iodide and sodium ethoxide on ethyl α -formylpropionate in alcoholic solution leads to the formation of a small amount of a neutral oil, which boils at $68\text{—}70^{\circ}$ under 20 mm. pressure, and is probably impure ethyl α -formylisobutyrate, as it gives the phenylhydrazine reaction for aldehydes.

Ethyl sodioformylacetate and benzenediazonium chloride react in

aqueous solution at 0° to form a brown oil which, on recrystallisation from alcohol, yields ethyl formazylcarboxylate. If the sodio-ester and diazonium chloride are rapidly mixed and immediately extracted with ether, the *phenylhydrazone* of ethyl formylglyoxylate,



is obtained as a viscid red oil. This is also formed by adding a cooled aqueous solution of benzenediazonium chloride to ethyl sodioformylacetate in absolute alcohol and pouring the mixture into ice-water. With phenylhydrazine in glacial acetic acid solution, it forms the *diphenylhydrazone*, $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_4$, which crystallises in yellow prisms and melts at $215\text{--}217^{\circ}$. The action of benzenediazonium chloride on ethyl sodio α -formylpropionate leads to the formation of the phenylhydrazone of ethyl pyruvate.

Ethyl sodioformylacetate and hydroxylamine hydrochloride react in cold aqueous solution to form the *oxime*, $\text{C}_5\text{H}_9\text{O}_3\text{N}$, which crystallises in long, white prisms and melts at $57\text{--}59^{\circ}$. The *oxime* of ethyl α -formyl propionate, $\text{C}_6\text{H}_{11}\text{O}_3\text{N}$, formed by the action of hydroxylamine on the ester in alcoholic solution, is an oil. The action of phenylhydrazine hydrochloride on ethyl α -formylpropionate in aqueous solution leads to the formation of 1-phenyl-4-methyl-5-pyrazolone, $\text{C}_{10}\text{H}_{10}\text{ON}_2$, which crystallises in concentric aggregates of small prisms, melts at $147\text{--}148^{\circ}$, and has weak acid and weak basic properties. With phenylhydrazine in ethereal solution, ethyl α -formylpropionate forms 1-phenyl-4-methyl-5-pyrazolone and an *isomeride*, which crystallises in plates and prisms and melts at $124\text{--}126^{\circ}$. G. Y.

Syntheses with Ethyl Sodioacetoacetate. ARTHUR MICHAEL (*Ber.*, 1905, **38**, 2083–2096. Compare Claisen and Haase, *Abstr.*, 1901, i, 118).—The author has prepared ethyl *O*-acetylacetoacetate by the action of acetyl chloride on the copper derivative of ethyl acetoacetate (Nef, *Abstr.*, 1893, i, 828), and by treating ethyl acetoacetate with acetyl chloride in pyridine solution (Claisen and Haase, *Abstr.*, 1900, i, 373); the latter process gave much the better yield. Both products boiled at $99\text{--}99.5^{\circ}$ (corr.) under 12 mm. pressure, and no difference could be detected in their chemical behaviour.

Ethyl diacetoacetate is not formed by the action of ethyl sodioacetoacetate on the *O*-acetylacetoacetate in cooled absolute ethereal solution, but is obtained as the chief product on adding ethyl sodioacetoacetate suspended in ether to an ethereal solution of acetyl chloride at -10° (compare Elion, *Rec. Trav. chim.*, 1884, **3**, 250). Contrary to Claisen's statement (*Abstr.*, 1894, i, 31), when ethyl sodioacetoacetate and *O*- β -carbethoxyacetoacetate are heated together in ethereal solution at 100° , no diacetoacetate, but only a small amount of a neutral oil boiling at 198° , is formed, and no interaction takes place between the copper derivative of ethyl acetoacetate and ethyl *O*- β -carbethoxyacetoacetate, when these are heated together in benzene solution at 100° . The formation of ethyl sodiodiacetoacetate by the action of acetyl chloride on ethyl sodioacetoacetate must be due to primary formation of the diacetoacetate and its subsequent interaction with unchanged sodioacetoacetate, or to the formation of a complex molecule from 2 mols. of ethyl sodioacetoacetate and 1 mol. of acetyl

chloride, and its subsequent decomposition with formation of ethyl acetoacetate and sodiodiacetoacetate and sodium acetate.

A *copper* derivative, $C_{10}H_{18}O_4Cu$, is formed by the action of cuprous chloride on ethyl sodioethylacetoacetate in absolute alcoholic solution (compare Wedel, Abstr., 1884, 834). It is a green powder which decomposes at 100° , or when quickly heated melts with effervescence at $188-189^\circ$, is insoluble in the ordinary solvents and is decomposed by warm water. When dried and treated with acetyl chloride in ethereal solution, the copper derivative yields a small amount of an oil which boils at 123° under 20 mm. pressure, and is identical with Elion's product from the action of acetyl chloride on ethyl sodioethylacetoacetate (*loc. cit.*).

When warmed with mercuric oxide, with or without ether, ethyl acetoacetate forms the crystalline mercuric derivative, $(C_6H_9O_2)_2Hg_2$, which is stable towards water or dilute acids, and is probably identical with Lippmann's compound (*Zeit. Chem.*, 1869, 12, 29).

In the preparation of ethyl alkylacetoacetates by the action of alkyl iodides on ethyl sodioacetoacetate, the unchanged acetoacetate is best removed by shaking the ethereal solution with dilute ammonia (compare Brühl, Abstr., 1904, i, 139). Three methods for the purification of alkylacetoacetates are described.

(1) The ester is stirred into a concentrated aqueous solution of potassium hydroxide cooled by ice-water, ether added, and the precipitate of ethyl potassioalkylacetoacetate filtered and washed with ether; the dialkylacetoacetate present is obtained by fractionation of the ethereal filtrate and washings, and the alkylacetoacetate by treatment of the precipitate with hydrochloric acid and fractionation of the liberated oil.

(2) The ester, dissolved in ether, is converted by sodium into the sodio-derivative and shaken with slightly less than 1 mol. of water; the insoluble hydrate formed in this manner is filtered, washed with ether, and decomposed by ice-cooled, dilute hydrochloric acid.

(3) The ester is treated with 1 mol. of sodium ethoxide dissolved in alcohol and with an alcoholic solution of cupric chloride until the precipitation is complete. The copper derivative, after being washed with alcohol and ice-water, is mixed with ice and decomposed by concentrated hydrochloric acid.

Of these methods, the first is the most easily carried out, but the second gives the best yields. Owing to hydrolysis of the ester, the purification is always accompanied by considerable loss of material (compare Wislicenus, Abstr., 1878, 402).

Ethyl dimethylacetoacetate is purified by shaking, and ethyl diethylacetoacetate, which is more stable, by boiling, with a 25 per cent. solution of potassium hydroxide. G. Y.

Action of Methyl and Ethyl Chloro-oxalates on Acetylacetone. R. TRIMBACH (*Bull. Soc. chim.*, 1905, [iii], 33, 693—695. Compare this vol., i, 323).—When methyl chloro-oxalate is added to the copper derivative of acetylacetone, dissolved in chloroform, *methyl acetylacetonxyloxalate*, $CHAc_2 \cdot CO \cdot CO_2Me$, is formed, and may be obtained as an oil by filtration and subsequent removal of the solvent

by distillation. This oil crystallises after a long time (a year was necessary in the initial preparation), but a more rapid separation of crystals may be induced by sowing the oil with the crystalline substance prepared previously. It crystallises in almost colourless needles or prisms, melts at 69° , and is readily soluble in alcohol or ether, less so in benzene. The solution in methyl alcohol attacks metallic copper, producing a green, crystalline substance. Water converts the ester into acetylacetone and oxalic acid. With phenylhydrazine, a substance is obtained which crystallises from boiling pyridine in colourless, silky needles, decomposes at 245° without melting, and may be sublimed. The product formed by the action of ethyl chloro-oxalate on acetylacetone is an uncrystallisable oil.

T. A. H.

Derivatives of Azelaic Acid. A. BOUCHONNET (*Compt. rend.*, 1905, 140, 1599—1601. Compare *Etaix*, Abstr., 1898, i, 124; *Derlou*, Abstr., 1898, i, 638; *Miller*, Abstr., 1899, i, 789, 791).—*Phenyl azelate*, $C_7H_{14}(CO_2Ph)_2$, prepared by the action of azelalyl chloride on phenol, forms flocculent masses of white needles, melts at $48-49^{\circ}$, and is slightly soluble in cold alcohol, readily so in ether, benzene, or carbon disulphide.

Thioazelallic acid, $C_7H_{14}(CO\cdot SH)_2$, obtained by heating phenyl azelate with sodium hydrogen sulphite in alcohol, forms bright yellow needles, melts at $72-74^{\circ}$, and is very soluble in ether, benzene, or alcohol. The sodium salt is very soluble in water. On adding lead acetate to an aqueous solution of the acid or the sodium salt, a yellowish-white precipitate, which rapidly becomes brown and then black, is produced. A similar reaction takes place with thiosuccinic acid.

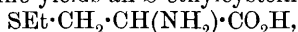
T. A. H.

Synthesis of the Lactone of Erythric Acid. ROBERT LESPIEAU (*Compt. rend.*, 1905, 141, 42—43. Compare Abstr., 1904, i, 471).—By boiling $\beta\gamma$ -dichlorobutyric acid with an aqueous solution of potassium carbonate, hydroxycrotonolactone, $\begin{array}{c} CH\cdot CH_2 \\ | \quad | \\ CH-CO \end{array} > O$, is produced (*loc. cit.*), and this, on oxidation with barium permanganate, furnishes erythrolactone, $\begin{array}{c} OH\cdot CH\cdot CH_2 \\ | \quad | \\ OH\cdot CH-CO \end{array} > O$. This crystallises from acetone in monoclinic prisms and from benzene in needles, melts at 91° , and is soluble in water, less so in alcohol or ether. T. A. H.

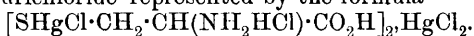
New Form of Thallium Tartrate. Isomorphous Mixtures of Thallium and Potassium Tartrates. JEAN HERBETTE (*Compt. rend.*, 1905, 140, 1649—1652).—When a concentrated solution of thallium tartrate is induced to crystallise by the addition of a crystal of potassium tartrate, monoclinic crystals of a variety of hydrated thallium tartrate, $[Tl_2C_4H_4O_6]_2\cdot H_2O$, are deposited. It is proposed to distinguish this as the *M* form. The crystals closely resemble those of potassium tartrate, and have $[a:b:c = 3.1056:1:3.9407; \beta = 90^{\circ}]$. The properties of the mixed crystals obtained by starting crystallisation in solutions of thallium tartrate of various concentrations

with potassium tartrate do not vary proportionally with the chemical composition; thus the angle β has the value 90° in thallium tartrate (72.2 per cent. of thallium), and falls to $88^\circ 36'$ in mixed crystals containing from 49.7 to 54.0 per cent. of thallium, and rises again to $89^\circ 10'$ in potassium tartrate. These mixed crystals are always richer in thallium than the solutions from which they separate. No crystals having the composition of a double salt were obtained. T. A. H.

Cysteine. II. CARL NEUBERG and PAUL MAYER (*Zeit. physiol. Chem.*, 1905, 44, 472—497. Compare Abstr., 1902, i, 743; Friedmann, *ibid.*, 731; 1903, i, 75, 301; E. Erlenmeyer, jun., *ibid.*, 1903, i, 791; this vol., i, 120; Gabriel, this vol., i, 266).—Two structurally isomeric cystines occur in nature, and these are termed *protein-cystine* and *calculus-cystine*, although urinary calculi often consist of a mixture of the two. Friedmann's cystine is pure protein-cystine; it crystallises in six-sided plates, has no definite melting point, but decomposes slowly at 258 — 261° , and it has $[\alpha]_D - 224^\circ$; its phenylcarbimide (Patten, Abstr., 1903, i, 792) melts at 160° (corr.), and when boiled with 25 per cent. hydrochloric acid yields an anhydride melting at 119° (corr.). Protein-cystine does not give Bamberger's hydroxamic acid test, but on treatment with nitrous acid yields the disulphide of β -thioglyceric acid. The benzoyl derivative (Brenzinger, Abstr., 1892, 1111) melts at 182 — 184° (corr.), the mercuric derivative has the composition $\text{Hg}[\text{CO}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2]_2\text{S}_2$, and is quite stable. Protein-cystine yields an *S*-ethylcysteine,



which melts at 228 — 230° , and a corresponding *benzyl* derivative melting at 226 — 228° (compare Brenzinger; Suter, Abstr., 1895, i, 624). Racemic protein-cystine crystallises in groups of needles resembling tyrosine, and the cysteine obtained by the reduction of protein-cystine yields a mercurichloride represented by the formula



Calculus-cystine crystallises in needles, melts and decomposes at 190 — 192° , is more readily soluble than its isomeride, and in hydrochloric acid solution has $[\alpha]_D - 206^\circ$. Its *phenylcarbimide* melts at 170 — 172° (corr.), and seems not to be decomposed when boiled with hydrochloric acid. Calculus-cystine gives Bamberger's hydroxamic acid test, and with nitrous acid undergoes complex decomposition. The *benzoyl* derivative melts at 157 — 159° (corr.), the mercuric derivative decomposes when dried, and has no definite composition. The *ethyl* derivative of calculus-cystine melts at 164 — 166° , and the *benzyl* derivative at 213° . Racemic calculus-cystine is amorphous, and the cysteine obtained on reducing calculus-cystine yields a mercurichloride,

$$\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}\begin{matrix} \text{S} \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{matrix} \text{Hg, HgCl}_2.$$

Although calculus-cystine resembles Gabriel's inactive *isocystine*, it is not certain that the two are identical.

The active protein- and calculus-cystines yield mixed crystals in the form of definite needles, which appear quite homogeneous. When heated with hydrochloric acid at 165° , both compounds are racemised.

J. J. S.

***d*-, *l*-, and *r*-Protein-cystines.** CARL NEUBERG and PAUL MAYER (*Zeit. physiol. Chem.*, 1905, **44**, 498—510. Compare preceding abstract, and Mauthner, *Abstr.*, 1902, **i**, 133).—The sodium derivative of natural protein-cystine, $S_2[CH_2 \cdot CH(NH_2) \cdot CO_2Na]_2$, is readily obtained by dissolving cystine in the requisite amount of *N*-sodium hydroxide, and on addition of certain metallic salts precipitates are obtained. The following have been analysed: *silver*, $C_6H_{10}O_4N_2S_2Ag_2$, *mercuric*, *lead*, *cadmium*, and *copper*, $C_6H_{10}O_4N_2S_2Cu$.

Mercuric acetate is a much better precipitant for cystine than either the sulphate or chloride.

A 50 per cent. yield of *r*-cystine is obtained when the natural product is heated with 15—20 times its weight of hydrochloric acid of sp. gr. 1.124 at 165° for 12—15 hours. It decomposes at the same temperature as the active compound, but is almost three times as soluble in water. The acid thus obtained is mainly the racemic and not the *meso*-form, since it can be resolved into active components by means of *Aspergillus niger*, the *d*-compound being left.

A *r*-cysteine has been obtained by reducing *r*-cystine. J. J. S.

Crystalline Form of Sodium Formaldehydesulphoxylate (Rongalit C.); A. OSANN (*Ber.*, 1905, **38**, 2290—2291. Compare Baumann, Thesmar, and Frossard, this vol., **i**, 260; Reinking, Dehnell, and Labhardt, this vol., **i**, 261; Bazlen, this vol., **ii**, 240).—Sodium formaldehydesulphoxylate dissolves in twice its weight of cold water; it crystallises in transparent, rhombo-holohedral plates [$a:b:c = 0.8421:1:0.6783$], which are easily obtained weighing as much as 400 grams. G. Y.

Aldehyde-ammonia. PAUL DUDEN, K. BOCK, and H. J. REID (*Ber.*, 1905, **38**, 2036—2044. Compare this vol., **i**, 558).—*Potassium β-amino-α-aci-dinitropropane*, $NH_2 \cdot CHMe \cdot C(NO_2):NO_2K$, prepared by the action of aldehyde-ammonia on potassium *aci*-dinitromethane, forms yellow crystals and decomposes at about 120°; acetaldehyde is evolved when its aqueous solution is boiled. The condensation is represented by the equation $NH_2 \cdot CHMe \cdot OH + NO_2 \cdot CH:NO_2K = H_2O + NH_2 \cdot CHMe \cdot C(NO_2):NO_2K$.

α-*Piperidyl-β-aci-dinitroethane*, $C_5NH_{10} \cdot CH_2 \cdot C(NO_2):NO_2H$, prepared from dinitromethane and 1-hydroxymethylpiperidine, separates from water in glistening needles and is stable when boiled with acids or alkalis. Its *acetyl* derivative forms colourless needles, which become green on exposure to air. Piperidyl-*aci*-dinitroethane is readily reduced by stannous chloride.

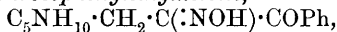
α-*Methylamino-β-aci-dinitroethane*, $C_3H_7O_4N_3$, separates from water in glistening plates and melts at 126—127°. *α*-*Dimethylamino-β-aci-dinitroethane*, $C_4H_9O_4N_3$, separates from water in hexagonal plates and melts at 115—117°.

Tetramethyldiaminonitropropane, $NO_2 \cdot CH(CH_2 \cdot NMe_2)_2$, prepared from acetaldehyde and hydroxymethyldimethylamine, melts at 58°. On exposure in a vacuum desiccator, it is quickly converted into a brown tar; its *hydrochloride* and *sodium* salt were prepared. Its aqueous solution is readily decomposed on boiling. When a solution of aniline in water

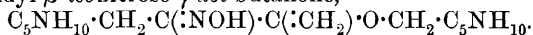
is added to its aqueous solution at 60—70°, *α,γ*-dianilino-*β*-nitropropane, $\text{NO}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{NPh})_2$, separates in yellow, quadratic leaflets, and melts at 157°. It is only slightly basic and is decomposed by acids or by alkalis much more slowly than is tetramethyldiaminonitropropane. Its *acetyl* derivative, $\text{NO}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{NPhAc})_2$, prepared by boiling with acetic anhydride, crystallises in prisms and melts at 129°. When dilute sulphuric acid is added to the solution of this diacetyl compound in an aqueous solution of sodium hydroxide, the *isomeric acetyl* derivative, $\text{C}(\text{CH}_2 \cdot \text{NPhAc})_2 \cdot \text{NO}_2\text{H}$, is precipitated; it gives a coloration with ferric chloride and is readily transformed into the former variety.

α,γ-Tetramethyldiamino-*β*-aminopropane, $\text{NH}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{NMe}_2)_2$, prepared by the reduction of a solution of tetramethyldiaminonitropropane in hydrochloric acid by stannous chloride, is a yellowish oil which boils at 174—175°.

α-Piperidyl-*β*-isonitrosophenylethylketone,

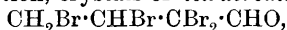


prepared by the action of *isonitrosoacetophenone* (1 mol.) on *N*-hydroxymethylpiperidine (1 mol.), crystallises in hexagonal plates, and melts and decomposes at 134—135°. The compound $\text{C}_{15}\text{H}_{27}\text{O}_2\text{N}_3$, prepared by the interaction of *isonitrosoacetophenone*, formaldehyde (2 mols.), and piperidine (2 mols.), separates from alcohol in red crystals and melts at 165°. It is probably the piperinomethyl ether of *α*-piperidyl-*β*-isonitroso-*γ*-*aci*-butanone,



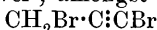
A. McK.

Bromination of Paraldehyde. PAUL FREUNDLER (*Compt rend.*, 1905, 140, 1693—1694).—Bromoacetaldehyde is readily obtained when paraldehyde is treated with bromine at −5° to 0°. It is not possible to introduce a second atom of bromine by operating at this temperature. If after addition of a second molecule of bromine the mass is allowed to become warm and is then poured into a mixture of ice and sodium carbonate solution, crystals of *tetrabromobutaldehyde*,



separate; this crystallises in large prisms, melts at 63—64°, boils at 145—147° under 13 mm. pressure, and is insoluble in water, but can be readily crystallised from ether or acetone. Tetrabromobutaldehyde is also formed when bromoacetaldehyde is treated successively with sulphuric acid and bromine, reaction taking place according to the equations $2\text{CH}_2\text{Br} \cdot \text{CHO} = \text{CH}_2\text{Br} \cdot \text{CH} \cdot \text{CBr} \cdot \text{CHO} + \text{H}_2\text{O}$; $\text{CH}_2\text{Br} \cdot \text{CH} \cdot \text{CBr} \cdot \text{CHO} + \text{Br}_2 = \text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CBr}_2 \cdot \text{CHO}$. It exhibits anomalous behaviour; it does not yield a hydrate, or a semicarbazone, or a bisulphite compound; it is not sensibly acted on by phosphorus pentabromide at 100°, or by concentrated aqueous alkali solutions. When warmed with ethyl alcohol, it decomposes completely, ethyl bromide, bromoacetaldehyde, bromoacetal, and probably ethyl bromoacetate being produced. Fuming nitric acid oxidises it in the cold with the formation of bromoacetic acid and hydrogen bromide. In ethereal solution, it is acted on by magnesium and some butaldehyde is formed. Crotonaldehyde is obtained from it by the action of zinc

and boiling water. When intimately mixed with large excess of sodium hydroxide and heated in a vacuum, a mixture of ethylene and acetylene bromides distils over; amongst these the bromide



was recognised. The residue contains formic acid.

H. M. D.

Crystals of *s*-Tetrachloroisopropyl Formal. GIUSEPPE CESÁRO (*Bull. Acad. roy. Belg.*, 1905, 128—129).—The author indicates that an error has been made in the determination of at least one of the crystallographic constants of this substance (Stappers, this vol., i, 261), and suggests that a re-examination of the crystals should be made.

T. A. H.

Preparation of Acraldehyde by the Boric Acid Method.

GEORG LOCKEMANN and OTTO LIESCHE (*J. pr. Chem.*, 1905, [ii], 71, 474—496. Compare Wohl and Neuberg, *Abstr.*, 1899, i, 565).—The authors describe and figure the apparatus used by them in the preparation of acraldehyde by Wohl and Neuberg's method, and in the fractional distillation of the products. With 1.5 kilos. of glycerol of sp. gr. 1.245, and 1 kilo. of boric acid, the yield of crude product amounts to 30—40 per cent. of the theoretical. After repeated distillation, a fraction is obtained boiling at 22—24°, consisting of acetaldehyde and representing 6—9 per cent. of the product, about 4—5 per cent. of which is obtained as fractions of high boiling point, containing substances of the nature of guaiacol and cresol. A fraction boiling at 26—27° contains, along with acetaldehyde, a substance which separates in slender, spear-like crystals, partially sublimes and partially melts at 60—65°, and may be metacraldehyde.

The gases evolved in the preparation of acraldehyde by this method consist of 48.6 per cent. of carbon monoxide, 13.9 of methane, 13.2 of hydrogen, 6.3 of oxygen, and 18.0 of nitrogen.

Contrary to Wohl and Neuberg's statement (*loc. cit.*), the polymerisation of acraldehyde is retarded by the presence of acetaldehyde, and takes place the more readily the greater the degree of purification. The polymerisation products are insoluble in cold 10 per cent. hydrochloric acid, and consist to the extent of 95 per cent. of disacryl resin, which is insoluble in cold alcohol, the remaining 5 per cent. consisting of hexacrylic acid.

Whilst the preparation of the acraldehyde by Wohl and Neuberg's method is accompanied by the formation of so many bye-products, no acetaldehyde is formed when glycerol is heated with potassium hydrogen sulphate, and, with the exception of sulphur dioxide, there are only traces of bye-products.

G. Y.

New β -Ketonic Aldehydes. FRANÇOIS COUTURIER and G. VIGNON (*Compt. rend.*, 1905, 140, 1695—1697).—A number of β -ketonic aldehydes of the type $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHO}$ or $\text{R}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ have been prepared by acting on a mixture of ethyl formate and a ketone with metallic sodium. The copper salts of the ketonic aldehydes, prepared by treating solutions of the sodium salts with acetic acid and copper acetate, were purified by crystallisation from ether. From

these the free aldehydes were obtained by the action of dilute sulphuric acid.

Diethylacetoacetaldehyde, $\text{CHEt}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$, is obtained from *as*-diethylacetone. The copper salt forms very dark blue crystals which melt at 68° . The free aldehyde boils at $60\text{--}62^\circ$ under 13 mm. or at $173\text{--}174^\circ$ under 760 mm. pressure without decomposing. The *semicarbazone* forms slender, white needles, which crystallise readily from absolute methyl alcohol and melt at 162° .

Trimethylacetoacetaldehyde, $\text{CMe}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$, is obtained from pinacolone. The copper salt crystallises in beautiful blue tablets which melt at $125\text{--}126^\circ$. The free aldehyde boils at $53\text{--}54^\circ$ under 13 mm. or at 148° under 760 mm. pressure without decomposing, reduces alkaline copper and silver solutions, and gives a red coloration with ferric chloride.

*iso*Propylacetoacetaldehyde, $\text{CH}_2\text{Pr}^i\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$, is obtained from methyl *isobutyl* ketone. The copper salt crystallises in blue needles which melt at $142\text{--}143^\circ$. The free aldehyde boils at $51\text{--}53^\circ$ under 13 mm. pressure without decomposition, decomposes when distilled under ordinary pressure, and is unstable at the ordinary temperature, gradually turns yellow and drops of water separate out from the liquid, indicating that condensation takes place.

*iso*Butylacetoacetaldehyde, $\text{CH}_2\text{Pr}^i\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$, is obtained from methyl *isoamyl* ketone. The copper salt melts at 120° . When this is decomposed with sulphuric acid, a red liquid is obtained which cannot be distilled even under reduced pressure without considerable decomposition. A small fraction of colourless liquid, which appears to be the free aldehyde, collects at $67\text{--}70^\circ$ under 13 mm. pressure.

In reference to the stability of these ketonic aldehydes, it appears that if a side-chain is attached to the carbon atom next to the ketone group the aldehydes are stable, but the stability rapidly diminishes if CH_2 groups are interposed between the ketone group and the ramification.

H. M. D.

Hydrogenation of Aldoximes. AUGUSTE MAILHE (*Compt. rend.*, 1905, 140, 1691—1693).—The aldoximes are reduced by free hydrogen at $180\text{--}220^\circ$ in presence of finely divided nickel. Primary amines are first formed according to the equation $\text{R}\cdot\text{CH}\cdot\text{NOH} + 2\text{H}_2 = \text{R}\cdot\text{CH}_2\cdot\text{NH}_2 + \text{H}_2\text{O}$. Under the influence of the nickel, the primary amines are, however, converted into secondary amines according to the equation $2\text{RCH}_2\cdot\text{NH}_2 = \text{NH}(\text{CH}_2\text{R})_2 + \text{NH}_3$. In some cases, small quantities of tertiary amines are also formed. Finely divided copper has a similar action to nickel. When reduced at $150\text{--}200^\circ$, acetaldoxime yields a considerable quantity of diethylamine and a small quantity of triethylamine.

When reduced at $210\text{--}220^\circ$, heptaldoxime yields primary, secondary, and tertiary heptylamines in the ratio 13:6:1. Heptylamine is a colourless liquid boiling at 153° ; with phenylcarbimide it yields phenylheptylcarbamide, which crystallises in prismatic needles melting at 63° . Diheptylamine forms colourless needles which melt at 30° ; it boils at 271° under 750 mm. pressure, is only slightly soluble in water, and yields a chloride and a carbonate which are both

deliquescent. Triheptylamine boils at 330° under 762 mm. pressure.

When the vapour of benzaldoxime is led by means of a current of hydrogen over finely divided copper at 220 — 230° , benzaldehyde is the chief product, but benzylamine, dibenzylamine, and tribenzylamine are also obtained. Under the influence of the heated copper, the benzaldoxime gives rise to benzaldehyde, water, and benzonitrile, and the amines are then produced by hydrogenation of the nitrile. When nickel is used instead of copper, toluene is the only reduction product obtained from benzaldoxime. H. M. D.

Electrolysis in Acetone and in Pyridine. MARIO G. LEVI and M. VOGHERA (*Gazzetta*, 1905, **35**, i, 277—290).—Electrolysis of an acetone solution of potassium thiocyanate between platinum electrodes yields, on the cathode, a whitish, crystalline crust, consisting of the potassium derivative of acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{K}$, and, on the anode, a yellow, flocculent substance, having a disagreeable odour, and probably formed by the oxidation of the thiocyanate ion.

Solutions of potassium, sodium, and ammonium iodides in acetone yield, on electrolysis, iodine at the anode, and, with potassium and sodium iodides, metallic derivatives of acetone, similar to that obtained with potassium thiocyanate at the cathode, whilst with ammonium iodide there is abundant evolution of gas at the cathode.

In the electrolysis of a pyridine solution of potassium thiocyanate, using an anode of porous carbon and a cathode of nickel, a black precipitate is formed at the anode, whilst at the cathode hydrogen is evolved, and a brownish-green, explosive substance deposited which dissolves in water without evolution of gas, giving a strongly alkaline solution, and consists probably of a potassium derivative of pyridine.

T. H. P.

Formation of Acetol [Acetylcarbinol] and Pyruvic Acid by Direct Oxidation of Acetone. PASTUREAU (*Compt. rend.*, 1905, **140**, 1591—1593).—When acetone is added to a solution of hydrogen peroxide (2 per cent.) in water, in presence of sulphuric or nitric acid, there are formed Baeyer and Villiger's acetone peroxide, $(\text{C}_3\text{H}_6\text{O}_2)_2$ (Abstr., 1900, i, 133), acetylcarbinol, and pyruvic acid. Acetone peroxide melts at 131.5° , is reduced by zinc or iron in presence of sodium hydroxide to acetone, and is also reconverted into the latter when heated with dilute sulphuric acid at 100° in closed tubes. When brominated, it yields a mixture of tetrabromoacetone and pentabromoacetone.

Similar products are formed by the action of sulphuric acid and hydrogen peroxide on other ketones.

T. A. H.

Derivatives of Butyrolin and Hexonoin. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1905, **140**, 1699—1700. Compare this vol., i, 560).—It is shown that butyrolin and hexonoin have both alcoholic and ketonic functions. Butyrolin forms an *oxime* boiling at 143° under 10 mm. pressure and a *semicarbazone* melting at 147° (corr.). It yields a *pyruvate* which boils at 134 — 138° under 12 mm. pressure, the *semi-*

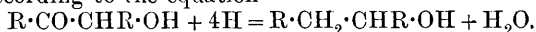
carbazone of which melts at 147° (corr.). Hexonoin yields a *semicarbazone* melting at 92°. When dehydrogenated by Sabatier and Senderens' method, butyrolin and hexonoin yield respectively the α -diketones, dibutyryl, and dihexoyl. Dibutyryl is a yellow liquid which boils at 168° under 760° mm. pressure, and yields a *dioxime* melting at 187° (corr.).

Dihexoyl boils at 110—115° under 15 mm. pressure, and yields a *dioxime* melting at 186° (corr.). When reduced by sodium in alcoholic solution, the diketones each yield a mixture of two isomeric symmetrical glycols.

α -*Octane- $\delta\epsilon$ -diol* is a liquid which boils at 115—120° under 10 mm. pressure. β -*Octane- $\delta\epsilon$ -diol* is crystalline, and melts at 125° (corr.). Both modifications are transformed into δ -octanone by heating in a sealed tube with dilute sulphuric acid at 180°.

α -*Dodecane- $\zeta\eta$ -diol* melts at 54° and boils at 155—160° under 10 mm. pressure. β -*Dodecane- $\zeta\eta$ -diol* melts at 135—136° (corr.). Both forms yield ζ -dodecanone under the influence of dilute sulphuric acid at 200°.

In addition to these glycols, univalent secondary alcohols are formed in the reduction of the diketones by means of sodium in alcoholic solution according to the equation



δ -*Octanol* is a mobile liquid with a pleasant odour which boils at 71° under 10 mm. pressure. It yields a *pyruvate* which boils at 108—116° under 10 mm. pressure, the *semicarbazone* of which melts at 96°. When oxidised with chromic acid, it yields δ -octanone, which boils at 165—168° under 760 mm. pressure and yields a *semicarbazone* melting at 100—101°.

ζ -*Dodecanol* is crystalline, melts at 30°, and boils at 119° under 9 mm. pressure. Its *pyruvate* boils at 150—152° under 10 mm. pressure and yields a *semicarbazone* melting at 93—94°. When oxidised by chromic acid, ζ -*dodecanone* is formed which melts at 9°, boils at 112° under 9 mm. pressure, and yields a liquid *semicarbazone* and an *oxime* which boils without decomposing at 147° under 10 mm. pressure.

H. M. D.

Isomeric Changes of some Dextrose Derivatives, and the Mutarotation of the Sugars. COENRAAD L. JUNGUS (*Zeit. physikal. Chem.*, 1905, 52, 97—108).—The bulk of this paper has already been reported (Abstr., 1903, i, 733; 1904, i, 651).—Dynamical experiments on the transformation of α - and β -methyl glucosides cannot settle the question whether the transformation is direct or indirect. Similar experiments with the two methyl galactosides in methyl alcohol containing hydrogen chloride show that for a given acid concentration the transformation of the methyl galactosides is 6—7 times as rapid as that of the methyl glucosides.

The author discusses the phenomena of mutarotation, and believes it to be conditioned by a transformation in which two stereoisomerides are concerned. Sometimes, as in the cases of dextrose and lactose, this transformation may be accompanied by hydration or dehydration, but in all cases the stereoisomeric change is the essential feature.

J. C. P.

Analogy between Starch coagulated by Amylocoagulase and Pea Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1905, 140, 1547—1549. Compare this vol., i, 312).—Pea starch when boiled with water does not form a paste, but 82—83 per cent. dissolves, and can be saccharified at 70°; about 22 per cent. is only soluble between 100° and 150°, and has properties closely analogous to those of amylocellulose or coagulated potato starch; it resists saccharification (compare Roux, this vol., i, 328), dissolves in potassium hydroxide, and the neutral solution gives an intense blue colour with iodine. Amylocoagulase is present both in the seed and pod of the green pea, and if potato starch paste is coagulated by malt extract or by pea extract, a quantity varying from 15·8 to 43·4 per cent. is converted into amylocellulose. M. A. W.

Acetylcelluloses. CARL HAEUSSERMANN (*Chem. Zeit.*, 1905, 29, 667. Compare Abstr., 1904, i, 144, 476).—Unlike penta-acetyl cellulose (Cross and Bevan, *Trans.*, 1890, 57, 2), the acetyl derivatives of hydrolysed cellulose obtained from Chemische Fabrik Sulzbach (D.R.-P. 118538 and 120713) are converted into nitric acid esters when treated at the ordinary temperature with nitric acid of sp. gr. 1·52. These esters may be denitrated by warming with an aqueous solution of sodium hydrosulphide, giving rise to a hydrocellulose, the identity of which is not yet completely established. Cellit, obtained from Bayer and Co., yields, on nitration, similar compounds though in much smaller quantity. P. H.

Estimation of Methoxyl Groups in some Lignocelluloses. ALWIN S. WHEELER (*Ber.*, 1905, 38, 2168—2169).—Methoxyl has been determined by Zeisel's method in the wood of 15 trees indigenous to North Carolina: they contained about 2·39 per cent. E. F. A.

Nitrogen in Gums. ALVISO B. STEVENS (*Amer. J. Pharm.*, 1905, 77, 255—260).—It is shown that all gums contain nitrogen, either in combination or in intimate association. This nitrogen cannot be converted into cyanogen by the usual reaction, but pyrrole or a pyrrole derivative is obtained when a gum is heated with potassium hydroxide. The true soluble gums possess in a varying degree the properties of enzymes, the activity of the enzyme being in proportion to the amount of nitrogen present in the gum. If enzymes and gums be two distinct substances, there is at present no known method of separating them. Since the gums or the acids prepared from them cannot be obtained entirely free from nitrogen, it follows that previous elementary analyses need revision, but it is possible that in some cases the amount of nitrogen present may have been too small to materially affect the relation of carbon, hydrogen, and oxygen. W. P. S.

Iodomercurates and Chloriodomercurate of Monomethylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1905, 140, 1697—1698).—The iodide $\text{NH}_3\text{MeI}, \text{HgI}_2$ separates in yellow needles from concentrated solutions containing mercuric iodide and methylammonium iodide in the molecular ratio 2:3. It melts at 173°, is

soluble in absolute alcohol or ether, very soluble in glacial acetic acid, but insoluble in chloroform, and is decomposed by water with separation of mercuric iodide. When heated, it undergoes decomposition into the component iodides.

The iodide $2\text{NH}_3\text{MeI}, \text{HgI}_2$ separates in large, yellow tablets when a hot concentrated solution containing mercuric iodide and methylammonium iodide in the molecular ratio 1:2 is allowed to cool. It melts at 221° , is insoluble in chloroform and ether, but dissolves in absolute alcohol, and is very soluble in warm acetic acid and in water.

The mixed haloid $2\text{NH}_3\text{MeCl}, \text{HgI}_2$ separates in colourless, well-formed, nacreous crystals from concentrated solutions containing mercuric iodide and methylammonium chloride in the molecular ratio 1:6. It melts at 139° , is soluble in absolute alcohol or acetic acid, but not in ether or in chloroform, and is decomposed by water with separation of mercuric iodide.

H. M. D.

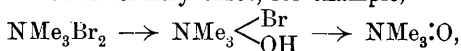
Additive Compounds of Tertiary Amines. ARTHUR HANTZSCH and WILHELM GRAF (*Ber.*, 1905, 38, 2154—2161).—The compound obtained by the addition of hydrogen chloride to trimethylamine oxide cannot have the oxonium constitution $\text{NMe}_3\cdot\text{OHCl}$, suggested by Willstätter and Iglaue (Abstr., 1900, i, 458), since aqueous solutions of the salts are only very slightly hydrolysed, and solutions of the oxide in water have a distinctly alkaline reaction. Both these properties are characteristic of ammonium rather than of oxonium derivatives, and the old formula for the salt, namely, $\text{OH}\cdot\text{NMe}_3\text{Cl}$, is retained. Since, however, this salt is not identical with the unstable hypothetical additive product of trimethylamine and hypochlorous acid (Willstätter), it is suggested that the two are isomeric, and that the trimethylamine oxide hydrochloride is trimethylhydroxyammonium chloride, $[\text{NMe}_3\text{OH}]\text{Cl}$, and the additive compound of hypochlorous acid and trimethylamine is trimethylchloroammonium hydroxide, $[\text{NMe}_3\text{Cl}]\text{OH}$. The primary product of the action of hypochlorous acid on trimethylamine is the hypochlorite of the base (as ions NMe_3H^+ and OCl^-), and the formation of such a salt is in harmony with the considerable increase in the electrical conductivity which is observed when the two solutions are mixed. In the decomposition of the hypochlorite to form dimethylchloroamine, a certain amount of hydrogen chloride is also formed.

Trimethylamine dibromide (Remsen and Norris, Abstr., 1896, i, 336) is readily obtained by mixing together the components in carbon disulphide solution, and crystallises from glacial acetic acid in reddish-yellow plates; it melts at $85\text{--}86^\circ$ to a brownish-yellow liquid, decomposes at 170° , and is also rapidly decomposed by moisture; it is insoluble in ether, carbon disulphide, or light petroleum, and dissolves sparingly in benzene or toluene. It readily liberates two equivalents of iodine from potassium iodide solution, and hence cannot have the formula given by Norris (Abstr., 1899, i, 663). No dibromide could be obtained from dimethylaniline, as even at -40° the bromine replaces the hydrogen in the para-position. *p*-Bromodimethylaniline dibromide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_2\text{Br}_2$, obtained from its components in

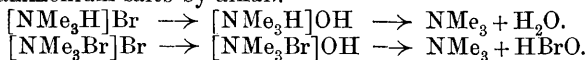
chloroform solution at low temperatures, crystallises in yellowish-red needles, melts and decomposes at about 100°, and is readily decomposed by water, alcohol, or concentrated sulphuric acid. The dibromides react with alkalis, yielding the free base, the alkali bromide, and hypobromous acid, and this can react with the base producing a bromoamide.

J. J. S.

Constitution of Ammonium Salts. ARTHUR HANTZSCH (*Ber.*, 1905, 38, 2161—2164).—The fact that alkalis do not transform trimethylamine dibromide and similar dibromides into hydroxybromides and oxides of tertiary bases, for example,



is used as an argument against the ordinary ammonium formula (quinquevalent nitrogen) for these and other ammonium compounds, and Werner's conceptions of the constitution are accepted, namely, a quadrivalent nitrogen atom, and the acid radicle being "extra radicle" and probably within the sphere of influence of the four groups attached to the nitrogen. Trimethylammonium chloride is written $[\text{NHMe}_3]\text{Cl}$, and the dibromide of trimethylamine $[\text{NBrMe}_3]\text{Br}$. The decomposition with alkalis is then analogous to the decomposition of alkyl ammonium salts by alkali.



The compounds trimethylhydroxyammonium bromide, $[\text{NMe}_3\text{OH}]\text{Br}$, and trimethylbromoammonium hydroxide, $[\text{NMe}_3\text{Br}]\text{OH}$, are termed coordination isomerides. A third isomeride is trimethylammonium hypobromite, $[\text{NMe}_3\text{H}]\text{OBr}$, which only exists in the form of its ions in solution. The action of hypochlorous acid on trimethylamine is supposed to consist partly in the addition of the ions Cl^+ and OH^- , and the formation of $[\text{NMe}_2\text{Cl}]\text{OH}$, which, like all ammonium hydroxides, readily decomposes partly into NMe_3 and HClO and partly into NMe_2Cl and CH_3OH . (Compare Willstätter and preceding abstract.)

J. J. S.

Action of Cyanogen Bromide on Hydrazine. GUIDO PELLIZZARI and CARLO CANTONI (*Gazzetta*, 1905, 35, i, 291—302).—The action of cyanogen chloride or bromide (1 mol.) on hydrazine (2 mols.) in aqueous solution yields:

(1) *Diaminoguanidine*, $\text{NH}\cdot\text{C}(\text{NH}\cdot\text{NH}_2)_2$, which is unstable and could not be isolated. Its *hydrobromide*, $\text{CH}_7\text{N}_5\cdot\text{HBr}$, is readily soluble in water and crystallises from alcohol in transparent, colourless plates which, in presence of the mother liquors, gradually change into small, opaque crystals melting and decomposing at 167°. The *picrate*, $\text{CH}_7\text{N}_5\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from water in slender needles melting and decomposing at 191°, and is soluble in alcohol. The *hydrochloride* separates from alcohol in small, white crystals which gradually become opaque and melt and decompose at 185°. The *platinichloride* separates from alcohol in minute, orange-yellow crystals melting at 172—173°. All the salts of diaminoguanidine energetically reduce Fehling's solution and ammoniacal silver nitrate solution in the cold.

(2) A small quantity of *p*-Di-iminohexahydrotetrazine (guanazine), $\text{NH:C} \begin{smallmatrix} \text{NH}\cdot\text{NH} \\ \text{NH}\cdot\text{NH} \end{smallmatrix} \text{C:NH}$, which is obtained as principal product when the cyanogen bromide and hydrazine are taken in molecular proportions and is also formed by the interaction of cyanogen bromide and diamino-guanidine hydrobromide. Its *hydrobromide*, $\text{C}_2\text{H}_6\text{N}_6\cdot\text{HBr}$, crystallises from water in a hard, white mass which melts and decomposes at 267° , and reduces Fehling's solution and ammoniacal silver nitrate solution when heated. The *picrate*, $\text{C}_2\text{H}_6\text{N}_6\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from water in long, yellow needles melting at 276° .

In acid aqueous solution the salts of diaminoguanidine react with benzaldehyde, giving the corresponding salts of *dibenzylidenediaminoguanidine*, $\text{NH:C}(\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$, which separates from benzene in yellow crystals melting at 180° and is readily soluble in alcohol. The *hydrobromide*, $\text{C}_{15}\text{H}_{15}\text{N}_6\cdot\text{HBr}$, crystallises from water in a felted mass of minute needles and from alcohol in tufts of acicular crystals melting at 243° . The *hydrochloride* crystallises from water in slender needles, melts at 230° , and is readily soluble in alcohol. Both these salts assume a yellowish-red colour in the air.

T. H. P.

Some Compounds of Guanidine with Sugars. ROBERT S. MORRELL and ALBERT BELLARS (*Proc. Camb. Phil. Soc.*, 1905, 13, 79—81).—When guanidine dissolved in alcohol is added to an alcoholic solution of either dextrose, levulose, maltose, galactose, or rhamnose, a microscopically crystalline precipitate is obtained which, in the case of the first three, is composed of three molecules of the sugar and one of guanidine, and in the case of galactose and rhamnose of molecular proportions of the two constituents; only the rhamnose compound could be crystallised. These substances, which all exhibit mutarotation, have a lower optical activity than the sugars from which they are derived. The dextrose and maltose compounds are decomposed completely by dilute hydrochloric acid. Picric acid precipitates guanidine picrate from aqueous solutions of the dextrose, levulose, galactose, and rhamnose compounds. When heated at 100° , these compounds melt and evolve alcohol, but not ammonia; the products formed are under investigation.

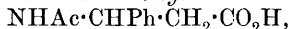
P. H.

***p*-Amino-acids.** THEODOR POSNER (*Ber.*, 1905, 38, 2316—2325).—The product obtained by the action of hydroxylamine on cinnamic acid is β -hydroxylamino- β -phenylpropionic acid, and not α -hydroxylamino- β -phenylpropionic acid, as formerly supposed by the author (*Abstr.*, 1904, i, 160). It is converted quantitatively into phenylisoxazolone identical with the product from hydroxylamine and ethyl benzoylacetate.

The compound described by Posen (*Abstr.*, 1873, 378) as β -amino- β -phenylpropionic acid is β -phenyl- β -lactamide, and is readily obtained as leaflets melting at 120 — 121° by the action of ammonia on β -bromo- β -phenylpropionic acid. Cinnamamide is formed by the action of sulphuric acid on β -phenyl- β -lactamide, and not lactimide, as is erroneously supposed by Posen (*loc. cit.*).

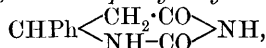
β -Amino- β -phenylpropionic acid (β -aminohydrocinnamic acid),

$\text{NH}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, formerly erroneously described by the author as α -aminohydrocinnamic acid, is prepared by prolonged boiling of cinnamic acid with an alcoholic solution of hydroxylamine. When heated above its melting point, it is decomposed into cinnamic acid and ammonia. The *monohydrochloride*, $\text{C}_9\text{H}_{11}\text{O}_2\text{N} \cdot \text{HCl}$, separates from a mixture of alcohol and ether in needles and melts at $217-218^\circ$. The *trihydrochloride*, $\text{C}_9\text{H}_{11}\text{O}_2\text{N} \cdot 3\text{HCl}$, separates from concentrated hydrochloric acid in needles which soften at 228° . The *sulphate*, $(\text{C}_9\text{H}_{11}\text{O}_2\text{N})_2 \cdot \text{H}_2\text{SO}_4$, forms glistening leaflets. The *copper*, *silver*, and *barium* salts are described. The *acetyl* derivative,



melts at $161-162^\circ$.

β -Carbamidohydrocinnamic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared from the free amino-acid (or its hydrochloride) and potassium cyanate, forms hexagonal prisms and melts and decomposes at 191° . When carefully heated, it forms *phenyldihydrouracil*,



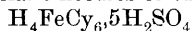
which separates from alcohol in needles and melts at $216-217^\circ$.

When the solution of β -carbamidohydrocinnamic acid in concentrated sulphuric acid is warmed at $60-70^\circ$ and then poured on to ice, a mixture of cinnamic acid and cyanuric acid is produced.

Phenyldihydrothiouracil, $\text{CHPh} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \text{NH} \cdot \text{CS} \end{array} \text{NH}$, was prepared from β -amino- β -phenylpropionic acid and potassium thiocyanate.

β -Hydroxy- β -phenylpropionic acid, prepared by the action of nitrous acid on β -amino- β -phenylpropionic acid, melts at 93° . Its acetyl derivative melts at 100.5° .
A. McK.

Compounds of Hydroferrocyanic and Sulphuric Acids. Sulpho-substitution in Complex Cyanides. Hydroxyferrocyanides. PAUL CHRÉTIEN (*Compt. rend.*, 1905, 141, 37-39).—When a saturated solution of hydroferrocyanic acid in sulphuric acid is slightly diluted with water so that the precipitate first formed redissolves, the mixture after a time deposits rhomboidal tablets of the compound $\text{H}_4\text{FeCy}_6 \cdot 7\text{H}_2\text{SO}_4$. By adding water until a permanent turbidity is produced, brilliant needles of the substance



are obtained. Both these substances revert to hydroferrocyanic acid on exposure to damp air.

When a solution of hydroferrocyanic acid (30 grams) in 100 grams of sulphuric acid of 66°B . is heated at $100-110^\circ$, the substance $2\text{H}_3\text{FeCy}_6 \cdot \text{HSO}_3 \cdot 7\text{H}_2\text{SO}_4$ is obtained, which crystallises in colourless lamellæ. This, when placed on a porous plate and exposed to air, is converted into the compound $\text{H}_3\text{FeCy}_6 \cdot \text{HSO}_3 \cdot \text{H}_2\text{O}$, which separates from alcohol in colourless, microscopic crystals. This is converted by barium hydroxide into barium ferrocyanide and sulphite, and, by saturation with barium carbonate in water and subsequent evaporation of the solution, into barium sulphite, ferrocyanide, and hydroxyferrocyanide.

With fuming sulphuric acid under similar conditions are obtained

needles of the substance $2\text{H}_2\text{FeCy}_6\text{SO}_2, 3\text{H}_2\text{S}_2\text{O}_7$, which dissolves in water producing a hissing noise, and when exposed on a porous plate to moist air absorbs an atom of oxygen and is converted into a mixture of the substance FeCy_6SO_2 (slightly yellow crystals stable in moist air) with the product $\text{H}_3\text{FeCy}_6\cdot\text{HSO}_3$, already described. When sodium hydroxide is added to a solution of the compound FeCy_6SO_2 in alcohol, the hydrated double salt $\text{Na}_3\text{FeCy}_6(\text{OH}), \text{Na}_2\text{SO}_4, 16\text{H}_2\text{O}$, crystallising in colourless needles, is obtained. Barium carbonate, under the same conditions, gives a precipitate of *barium hydroxyferrocyanide*, $\text{Ba}_2(\text{FeCy}_6\cdot\text{OH})_2, 4\text{H}_2\text{O}$. These products give blue colorations with ferric but not with ferrous salts.

T. A. H.

Theory of Carbamide Formation. HANS EPPINGER (*Beitr. chem. Physiol. Path.*, 1905, 6, 481—491. Compare Hofmeister, *Abstr.*, 1897, ii, 335; Halsey, 1898, ii, 529; Schwarz, 1899, ii, 165; Plimmer, 1904, i, 538; this vol., i, 162).—When amino-acids are oxidised with permanganate in the presence of acid, hydrogen cyanide is formed, but no cyanic acid.

Glycine, when oxidised with permanganate, yields carbamide, and as an intermediate product glyoxylic acid, although neither glyoxylic acid itself nor aminoglyoxylic acid yields carbamide on oxidation in the presence of ammonia.

A distinct carbylamine odour is observed when glycine is oxidised with permanganate in the presence of aniline, and the same odour is observed when lactic, tartaric, oxalic acid, or methyl alcohol is used in place of glyoxylic acid. Small amounts of phenyl- and diphenyl-carbamide are also formed, and in the presence of methylamine small amounts of methyl- and dimethyl-carbamide. There appears to be no general parallelism between the compounds which yield carbamide on oxidation in presence of ammonia and those which yield a carbylamine odour when oxidised in presence of aniline.

A list, complete to date, is given of those substances which yield carbamide when oxidised in the presence of ammonia.

J. J. S.

Action of Ammonia on Sulphuryl Chloride. BERNHARD C. STUER (*Ber.*, 1905, 38, 2326).—Hantzsch and the author (this vol., ii, 312) stated that melanurenic acid is not formed together with carbamide, cyanuric acid, and cyamelide when dry ammonia is passed into a solution of carbonyl chloride in light petroleum at 0° . The author now finds, however, that melanurenic acid is formed under these conditions.

A. McK.

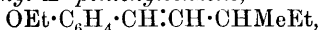
Syntheses by means of Zinc Chloride. [*iso*Butyltoluene.] STANISLAS NIEMCZYCKI (*Bull. Acad. Sci. Cracow*, 1905, 2—5).—Goldschmidt's supposed *p*-isobutyltoluene (*Abstr.*, 1882, 952), formed by heating toluene and isobutylalcohol with zinc chloride, yields on nitration 2:4:6-trinitro-3-isobutyltoluene (Bauer, *Abstr.*, 1890, 1401; 1891, 1464), and is therefore *m*-isobutyltoluene.

G. Y.

Optically Active Benzene Hydrocarbons and Phenolic Ethers. AUGUST KLAGES and RICHARD SAUTTER (*Ber.*, 1905, 38, 2312—2315. Compare *Abstr.*, 1904, i, 302).—d-1-iso*Propyl*-3- γ -methyl-

Δ^{α} -pentenylbenzene, $C_6H_4Pr \cdot CH:CH \cdot CHMeEt$, prepared by the action of magnesium *d*-amyl iodide on *p*-isopropylbenzaldehyde, boils at $139-140.5^{\circ}$ under 9.5 mm. pressure, has the sp. gr. 0.8801 at $16^{\circ}/4^{\circ}$, n_D 1.5181 and $[\alpha]_D + 41.89^{\circ}$ at 16° . It decolorises permanganate. Its dibromide is dextrorotatory, separates from aqueous alcohol in slender needles, and melts at $95-96^{\circ}$. When reduced by sodium and absolute alcohol, *d*-1-isopropyl-3- γ -methylpentenylbenzene forms *d*-1-isopropyl-3- γ -methylamylbenzene, $C_6H_4Pr \cdot CH_2 \cdot CH_2 \cdot CHMeEt$, which boils at $131-132^{\circ}$ under 10.2 mm. pressure or at 265° under 748 mm. pressure, has the sp. gr. 0.8632 at $15.5^{\circ}/4^{\circ}$, n_D 1.4921 and $[\alpha]_D + 15.91^{\circ}$ at 15.5° .

d-2-Ethoxy-1- γ -methyl- Δ^{α} -pentenylbenzene,



prepared by the action of magnesium *d*-amyl iodide on *o*-ethoxybenzaldehyde, boils at $135.5-137^{\circ}$ under 9.2 mm. pressure, has the sp. gr. 0.9406 at $15^{\circ}/4^{\circ}$, n_D 1.5297 and $[\alpha]_D + 40.97^{\circ}$ at 15° . When reduced by sodium and absolute alcohol, it forms *d*-2-ethoxy-1- γ -methylamylbenzene, $OEt \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CHMeEt$, which boils at $126-127^{\circ}$ under 9 mm. pressure or at 260° under 753 mm. pressure, has the sp. gr. 0.9119 at $16^{\circ}/4^{\circ}$, n_D 1.4937 and $[\alpha]_D + 14.99^{\circ}$ at 16° . When converted into its sulphonic acid and then regenerated by heating the latter with water and a little hydrochloric acid for 5 hours at 160° , no racemisation has occurred.

The influence of the double linking on optical activity is exemplified in the compounds examined. A. McK.

Derivatives of *p*-Dichloro-, *p*-Dibromo-, and *v-m*-Dibromiodobenzene with Polyvalent Iodine. CONRAD WILLGERODT (*J. pr. Chem.*, 1905, [ii], 71, 540-566).—[With ALBERT LANDENBERGER.]—*p*-Dichloriodobenzene (Herschmann, Abstr., 1894, i, 330), formed by the action of potassium iodide on diazotised *p*-dichloroaniline, crystallises in large, transparent, rhombic plates which become yellow on exposure to light, melts at 21° , and distils at $255-256^{\circ}$ under 742 mm. pressure. *p*-Dichlorobenzene iodochloride, $C_6H_3Cl_2 \cdot ICl_2$, formed by the action of chlorine on *p*-dichloriodobenzene in cooled glacial acetic acid solution, crystallises in small plates, decomposes at $108-110^{\circ}$, and is converted by 10 per cent. aqueous sodium hydroxide into the corresponding iodoso-compound, which is obtained as a yellow, amorphous powder commencing to decompose at 100° , and melting with effervescence at 193° ; the acetate, $C_6H_3Cl_2 \cdot I(OAc)_2$, forms white needles or prisms and melts and decomposes at 175° ; the basic sulphate, $[C_6H_3Cl_2 \cdot I(OH)]_2SO_4$, forms an amorphous powder melting and decomposing at 142° ; after several weeks, the filtrate from the basic sulphate deposits a crystalline substance melting and decomposing at 150° ; the basic chromate, $[C_6H_3Cl_2 \cdot I(OH)]_2CrO_4$, forms an orange-coloured, amorphous powder, which detonates at $69-70^{\circ}$; the basic nitrate, $C_6H_3Cl_2 \cdot I(OH) \cdot NO_3$, is obtained as a white powder, which melts and decomposes at $126-128^{\circ}$. *p*-Dichloriodoxybenzene, $C_6H_3Cl_2 \cdot IO_2$, is formed by treating the iodoso-compound with a current of steam, or by the action of aqueous

sodium hypochlorite on the iodochloride; it crystallises in microscopic, white needles and decomposes with slight detonation at 230° .

Di-p-dichlorophenyliodonium hydroxide is obtained as an alkaline solution which decomposes on evaporation; the chloride, $\text{I}(\text{C}_6\text{H}_3\text{Cl}_2)_2\text{Cl}$, crystallises in small prisms and melts at 176° ; the *bromide* forms an amorphous, white powder and melts at 170° ; the *iodide* is obtained as a yellow precipitate melting at 138° ; the *nitrate* forms microscopic needles and melts at 176° ; the orange-coloured, amorphous *dichromate* detonates at 148 – 150° ; the *platinichloride* crystallises in flesh-coloured needles and melts and decomposes at 240° .

Phenyl-p-dichlorophenyliodonium hydroxide, $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{IPh}\cdot\text{OH}$, is obtained by treating a mixture of iodosobenzene and *p*-dichloriodobenzene with moist silver oxide. The *chloride* crystallises in prisms and melts at 214° ; the *bromide* forms white prisms and melts at 194° ; the *iodide* crystallises in white prisms and melts at 132° ; the *dichromate* explodes at 158° ; the *platinichloride* forms microscopic, yellow needles and melts and decomposes at 198° ; the *mercurichloride* forms small, colourless crystals and melts at 157° .

p-Dichlorophenyl-p-tolyliodonium hydroxide, $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{I}(\text{C}_7\text{H}_7)\cdot\text{OH}$, formed from *p*-iodosotoluene and *p*-dichloriodobenzene, is known only in alkaline aqueous solution. The *chloride* crystallises in white needles melting at 210° ; the *bromide* is obtained as a white precipitate which melts at 188° ; the yellow *iodide* melts at 128° ; the orange-coloured, amorphous *dichromate* detonates at 165° ; the *platinichloride* crystallises in scarlet prisms and melts and decomposes at 183° .

p-Dichlorophenylp-dichloriodophenyliodonium hydroxide, formed from *p*-dichloriodosobenzene by Hartmann and Meyer's method (Abstr., 1894, i, 242), is known only in its aqueous solution, which is alkaline and almost odourless. The *chloride*, $\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{I}\cdot\text{I}(\text{C}_6\text{H}_3\text{Cl}_2)\text{Cl}$, is amorphous, sinters at 125° , and melts at 156° ; the *bromide* sinters at 125° and melts at 148° ; the yellow *iodide* sinters at 110° and melts at 124 – 125° ; the scarlet, amorphous *dichromate* sinters at 100° and decomposes without melting at higher temperatures; the *platinichloride* crystallises in brown prisms and melts at 198° .

p-Dichlorophenyldichloroethyliodonium chloride, $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{ICl}\cdot\text{C}_2\text{H}_3\text{Cl}_2$, prepared by the action of *p*-dichlorophenyl iodochloride on a compound of silver acetylide and silver chloride suspended in water (see Willgerodt and Roggatz, Abstr., 1900, i, 432), is obtained on evaporation of its aqueous solution in transparent prisms, or on addition of concentrated hydrochloric acid as a white, microcrystalline precipitate; it melts and decomposes at 178° ; the *bromide* melts and decomposes at 163° ; the *iodide* melts and detonates at 104° ; the *dichromate* forms small, red needles, and detonates at 90 – 92° ; the *platinichloride* forms brown needles and melts and decomposes at -147° .

[With REINHOLD THIELE.]—*p*-Dibromiodobenzene, formed from *p*-dibromoaniline, crystallises in nodular aggregates of colourless needles and melts at 38° (compare Istrati and Edeleanu, *Bull. Soc. chim.*, 1859, 1, 205). *p*-Dibromobenzene iodochloride, $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{ICl}_2$, formed by chlorination of *p*-dibromiodobenzene in glacial acetic acid chloride, forms yellow, unstable crystals, decomposes at 100° and is completely melted at 106° . When treated with 5–6 per cent.

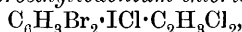
aqueous sodium hydroxide, it yields the corresponding *iodoso*-compound, $C_6H_3Br_2 \cdot IO$, which melts and decomposes at 108° ; the *acetate* crystallises in glistening, silvery leaflets and melts at 168° ; the *basic nitrate* forms a white powder which detonates at 120° ; the *basic sulphate* is obtained as a white powder which melts and decomposes at 122° ; the *basic chromate* melts and decomposes at 43° . *p*-Dibromo-iodoxybenzene, $C_6H_3Br_2 \cdot IO_2$, is formed by the action of steam on the *iodoso*-compound, or by the action of calcium or sodium hypochlorite on the *iodochloride*; it is obtained as a white, amorphous powder which explodes at 218° .

Di-p-dibromophenyliodonium hydroxide, $I(C_6H_3Br_2)_2 \cdot OH$, is known only in its aqueous alkaline solution; the *chloride* forms a white powder, which melts and decomposes at 185° ; the *bromide* melts at 161° ; the yellow, amorphous *iodide* decomposes at 101 – 102° ; the *dichromate* is a yellow, amorphous powder which decomposes at 104 – 106° ; the orange-coloured *platinichloride* melts and decomposes at 254° .

Phenyl-p-dibromophenyliodonium hydroxide, $C_6H_3Br_2 \cdot IPh \cdot OH$, forms an alkaline, aqueous solution; the white, amorphous *chloride* sinters at 150° and decomposes at 165° ; the white, amorphous *bromide* melts at 177° ; the *iodide*, obtained as a yellow, amorphous precipitate, melts and decomposes at 142° ; the orange-coloured *dichromate* explodes at 141° ; the orange-coloured *platinichloride* decomposes at 186 – 187° .

p-Dibromophenyl-*p*-tolyliodonium hydroxide forms an alkaline, aqueous solution; the white *chloride* melts at 195° ; the white, amorphous *bromide* melts at 171° ; the yellow, amorphous *iodide* melts and decomposes at 131° ; the orange-yellow *dichromate* melts and explodes at 148° ; the orange-coloured *platinichloride* melts at 191° ; the *mercurichloride* forms a white, soluble powder which melts at 123° .

p-Dibromophenyldichloroethyliodonium chloride,



is known only in solution; the white, amorphous *bromide* melts at 148° ; the *iodide* melts and decomposes at 89° ; the reddish-yellow, amorphous *dichromate* melts and decomposes at 86° ; the orange-coloured *platinichloride* melts and decomposes at 148° .

[With PAUL FRISCHMUTH.]—*v-m*-Dibromiodobenzene, $C_6H_3Br_2I$, formed from 2:6-dibromoaniline, crystallises in colourless, hexagonal prisms, and melts at 99° . 1:3-Dibromobenzene 2-iodochloride, $C_6H_3Br_2 \cdot ICl_2$, crystallises in small, yellow needles, melts and intumesces at 91° , and is converted by aqueous sodium hydroxide into 1:3-dibromo-2-iodosobenzene, $C_6H_3Br_2 \cdot IO$, which forms a brownish-yellow, amorphous powder, melts and detonates at 95° , and gradually loses oxygen, forming 1:3-dibromo-2-iodobenzene. The *acetate*, $C_6H_3Br_2 \cdot I(OAc)_2$, forms small, white crystals, melting at 170° ; the *basic nitrate* is a yellow, crystalline powder which detonates slightly at 114° ; the *basic iodate*, $C_6H_3Br_2 \cdot I(OH) \cdot IO_3$, forms a white powder, commences to turn brown at 160° and melts and decomposes at 240° ; the *basic sulphate* is a white, amorphous powder which explodes at 150 – 165° ; the brown, crystalline *basic chromate* decomposes at 70° .

Neither iodoxy- nor iodonium compounds could be obtained from 1:3-dibromo-2-iodobenzene or the corresponding iodoso-compound or its salts. G. Y.

Isomeric Dichloronitrobenzenes. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 668—673. Compare Abstr., 1904, i, 304).—Of the six dichloronitrobenzenes, four have been obtained in such a form that their crystallographic examination in detail has been possible. These four are (a) 1:2-dichloro-3-nitrobenzene, rhombic, $[a:b:c = 0.6472:1:0.2780]$; (b) 1:3-dichloro-2-nitrobenzene, monoclinic, $[a:b:c = 0.6696:1:0.4149; \beta = 87^{\circ}51']$; (c) 1:3-dichloro-5-nitrobenzene, monoclinic, $[a:b = 0.5940:1; \beta = 58^{\circ}43']$; and (d) 1:4-dichloro-2-nitrobenzene, triclinic, $[a:b:c = 0.8702:1:0.8239; \alpha = 92^{\circ}48'; \beta = 112^{\circ}51'; \gamma = 60^{\circ}5']$. The orthodichloro-derivatives are both rhombic; the metadichloro-derivatives are probably all monoclinic, and the paradichloro-derivative is triclinic. J. C. P.

Friedel and Crafts' Reaction. VII. Action of Sulphur or Sulphur Chlorides on Benzene in Presence of Aluminium Chloride. JACOB BOESEKEN (*Rec. Trav. chim.*, 1905, 24, 209—222. Compare this vol., i, 423, 424).—Sulphur monochloride, S_2Cl_2 , and sulphur dichloride, SCl_2 , do not form additive compounds with aluminium chloride. When the former reacts with aluminium chloride in presence of sulphuryl chloride, Ruff's additive compound, $AlCl_3 \cdot SCl_2$, separates (Abstr., 1901, ii, 500). With benzene in presence of aluminium chloride, sulphur monochloride yields the theoretical quantity of diphenyl sulphide, required by the equation $S_2Cl_2 + 2C_6H_6 + AlCl_3 = Ph_2S \cdot AlCl_3 + S + 2HCl$. The formation of diphenyl sulphide in this reaction is a further proof of the unsymmetrical constitution, $S \cdot SCl_2$, of sulphur monochloride (compare Lippman and Pollak, Abstr., 1901, i, 690).

When benzene is treated with sulphur dichloride in presence of aluminium chloride at 0° , diphenyl sulphide (b. p. 156° under 8 mm. and 226° under 760 mm. pressure) is almost the sole product, but at 60° there are also produced chlorobenzene and thianthrene (diphenylene disulphide), the formation of these being due to the decomposition of the sulphur chloride into the monochloride and chlorine, which then attack the benzene (compare Krafft and Lyon, Abstr., 1896, i, 297). These reactions lend support to the view that sulphur dichloride exists at low temperatures (compare Ruff and Fischer, Abstr., 1903, ii, 204, and Aten, *Thesis*, 1904).

When benzene is treated with sulphur in presence of aluminium chloride, diphenyl sulphide, thianthrene, and hydrogen sulphide are the chief products, but there is also formed a small quantity of a colourless substance, which melts at 315° and gives a green coloration when heated with aluminium chloride. Diphenyl sulphide gives a colourless additive product, $Ph_2S \cdot AlCl_3$, with aluminium chloride, whilst the corresponding thianthrene compound, $C_{12}H_8S_2 \cdot AlCl_3$, is blue. These two substances also give respectively colourless and blue derivatives with sulphuric acid and bromine, so that possibly the latter derivatives may also be additive products. T. A. H.

Formation of Anhydrides of Sulphonic Acids by the Action of Sulphonic Chlorides on Silver Cyanate. OTTO C. BILLETER (*Ber.*, 1905, **38**, 2015—2020. Compare this vol., i, 560).—The author has previously shown that when benzenesulphonic chloride is heated at 140° with silver cyanate, a mixture of unchanged chloride and benzenesulphoncarbimide is formed (*Abstr.*, 1904, i, 397), whilst a brown liquid solidifying to a mass of leaflets remains. The latter product has now been examined, and from it *benzenesulphonic anhydride*, $C_{12}H_{10}O_5S_2$, melting at 92° and boiling and decomposing at 240° under 10 mm. pressure, has been isolated. Its behaviour towards water and alcohol was studied quantitatively.

Benzenesulphonic anhydride is described by Abrahall (*Trans.*, 1873, **26**, 606) as having been obtained by the action of benzenesulphonic chloride on silver benzenesulphonate; this product is, however, the free acid.

By the action of silver cyanate on methanesulphonic chloride, pure methanesulphonic anhydride was not isolated; by the action of ether on the crude product, *ethyl methanesulphonate*, $C_3H_8O_3S$, boiling at 85 — 86° under 10 mm. pressure, was prepared.

Methanesulphonic chloride, prepared by the action of phosphorus pentachloride on sodium methanesulphonate, boils at 161 — 161.5° under 730 mm. pressure and has the sp. gr. 1.48053 at $18^{\circ}/4^{\circ}$ and 1.46973 at $25^{\circ}/4^{\circ}$. Methanesulphonic acid, prepared by the action of water on methanesulphonic chloride, boils at 167 — 167.5° under 10 mm. pressure and has a sp. gr. 1.4812 at $18^{\circ}/4^{\circ}$.

Methanesulphonic anhydride, $C_2H_6O_5S_2$, prepared by heating methylsulphonic chloride with silver methylsulphonate for 3 hours at 160° , separates from ether in prisms and melts at 71° . A. McK.

Double Salts of Palladous Chloride and Bromide. ALEXANDER GUTBIER (*Ber.*, 1905, **38**, 2105—2107).—Double salts of palladous chloride and bromide with hydrochlorides or hydrobromides of organic bases are formed by adding small amounts of the latter to an excess of the palladous salt in aqueous solution. The double salts can be recrystallised from dilute hydrochloric or hydrobromic acid respectively.

Aniline palladous chloride, $(NH_3PhCl)_2PdCl_2$, is obtained as a golden precipitate; the bromide crystallises in brown leaflets. *o-Toluidine palladous chloride*, $(NH_3C_7H_7Cl)_2PdCl_2$, crystallises in glistening, yellowish-brown leaflets; the bromide forms glistening, reddish-brown needles. *p-Toluidine palladous chloride* crystallises in brown, pointed needles; the bromide forms reddish-brown needles. G. Y.

Derivatives of Palladosammine Chloride and Bromide. ALEXANDER GUTBIER (*Ber.*, 1905, **38**, 2107—2111. Compare Hardin, *Abstr.*, 1900, ii, 85).—Derivatives of palladosammine chloride or bromide are formed by adding small amounts of palladous chloride or bromide solution to an excess of the hydrochloride or hydrobromide of an organic base dissolved in water and warming the reacting mixture.

Diphenylpalladosammine chloride, $Pd(NH_3Ph)_2Cl_2$, forms an insoluble, yellow, laminated precipitate, and, when warmed with concen-

trated ammonia, is converted into aniline and palladosammine chloride. When treated with ammonia, diphenylpalladosammine bromide yields aniline and palladosammine bromide. *Di-o-tolylpalladosammine chloride*, $\text{Pd}(\text{C}_7\text{H}_7\cdot\text{NH}_2)_2\text{Cl}_2$, crystallises in glistening, golden scales. *Di-o-tolylpalladosammine bromide* crystallises in small, glistening needles. *Di-p-tolylpalladosammine chloride* crystallises in glistening, golden leaflets. *Di-p-tolylpalladosammine bromide* forms small, glistening needles. When warmed with aqueous ammonia, the tolylpalladosammine chlorides and bromides yield the toluidine and palladosammine chloride or bromide respectively.

These derivatives of palladosammine chloride or bromide can be formed also by the action of an alcoholic solution of the base on palladous chloride or bromide. G. Y.

Action of Chloroacetates on Magnesium Haloid Derivatives of Aniline. F. BODROUX (*Compt. rend.*, 1905, 140, 1597—1598. Compare Abstr., 1904, i, 662).—When magnesium phenylamine iodide, $\text{NHPh}\cdot\text{MgI}$ (Meunier, Abstr., 1903, i, 544), is treated with ethyl chloroacetate, there are formed iodoacetanilide, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}_2\text{I}$ (m. p. 143—144°) and ethyl iodoacetate. The latter reacts feebly with magnesium phenylamine iodide, forming tarry products. With magnesium phenylamine bromide, ethyl chloroacetate yields only chloroacetanilide. When ethyl dichloroacetate or trichloroacetate reacts with magnesium phenylamine iodide, dichloroacetanilide or trichloroacetanilide are produced respectively.

Ethyl chloroacetate reacts similarly with magnesium ethiodide, forming ethyl iodoacetate (b. p. 178—180°). T. A. H.

Derivatives of Mesoxalic Esters. C. SCHMITT (*Compt. rend.*, 1905, 141, 48—49. Compare this vol., i, 508, and Curtiss, this vol., i, 507).—*Methyl mesoxalate bisanilide*, $\text{C}(\text{NHPh})_2(\text{CO}_2\text{Me})_2$, obtained by condensing methyl mesoxalate with aniline dissolved in acetic acid, crystallises in slender, white needles, melts at 113·5°, and is soluble in ether or alcohol, slightly so in light petroleum or toluene. It develops a blue coloration with sulphuric acid and potassium dichromate. *Ethyl mesoxalate bisanilide* melts at 103°. The corresponding *toluidine* derivative of the methyl ester begins to decompose at 120°, and melts finally at 172°. Hydrochloric acid hydrolyses these compounds into their generators, but alkalis have no action even on warming. T. A. H.

o-Nitrobenzyltoluidine. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 666—668).—Although this compound differs in symmetry from Nordenskiöld's para-derivative, the analogy of the two isomerides may be traced in the value of $b:c$.

o-Nitrobenzyl-*p*-toluidine : $a:b:c = 1:1:0\cdot623$.

o-Nitrobenzyl-*o*-toluidine : $a:b:c = 0\cdot8552:1:0\cdot6138$. J. C. P.

Action of Sulphite on Aromatic Amino- and Hydroxy-compounds. III. Preparation of Arylated β -Naphthylamines and of $\beta\beta'$ -Dinaphthylamines. HANS TH. BUCHERER and A. STOHMANN (*J. pr. Chem.*, 1905, [ii], 71, 433—451. Compare Abstr., 1903, i, 627; 1904, i, 309, 395; this vol., i, 48).—Whilst

α -naphthol-4-sulphonic acid and resorcinol, when heated with sodium hydrogen sulphite and aniline, yield the sulphites but not the secondary amines, secondary β -naphthylamines are formed by the interaction of β -naphthyl derivatives with aromatic amines.

$\beta\beta'$ -Dinaphthylamine-6:6-disulphonic acid (D.R.-P. 114974) is formed when 1 mol. of β -naphthol-6-sulphonic acid is heated with $1\frac{1}{2}$ mols. of ammonium sulphite.

β -Naphthylamine-5-sulphonic acid differs in its behaviour from the other β -naphthyl derivatives; even in presence of 10–20 mols. of sodium hydrogen sulphite, β -naphthylamine-5-sulphonic acid forms large amounts of $\beta\beta'$ -dinaphthylamine-5:5'-disulphonic acid, which is soluble in water and, on prolonged boiling with an excess of sulphite, appears to yield traces of β -naphthol-5-sulphonic acid and ammonia. When boiled for 24 hours with sodium hydrogen sulphite and aniline in aqueous solution, β -naphthylamine-5-sulphonic acid is largely regained unchanged from the precipitate obtained on acidification.

The formation of secondary amines by this method is confined to those β -naphthols which are capable of forming sulphites. Anthraquinone derivatives do not enter into the reaction. On the other hand, the action depends on the nature of the arylamine as well as on that of the naphthyl derivative; *p*-aminophenol and *p*-phenylenediamine enter into the reaction most easily, benzidine, β -naphthylamine, and β -naphthylamine ethers least so, whilst between these extremes lie aniline, *p*-phenetidine, sulphanilic and metanilic acids, *o*- and *p*-toluidines, pararosanine, and xylidine.

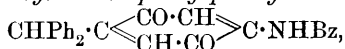
Details are given as to the proportions of β -naphthyl derivative, sodium hydrogen sulphite, arylamine, and water which give the best yields in particular cases.

It is found that, in the preparation of β -anilinonaphthalene-6-sulphonic acid with addition to the reaction mixture of a weight of dimethylaniline equal to that of the aniline, the yield is increased from 50 to 86, and with twice that weight of dimethylaniline, to 100 per cent. The results of solubility determinations of β -arylamino-naphthalenesulphonic acids in water show striking differences in the solubilities of place isomerides and other closely related compounds.

G. Y.

Derivatives of *p*-Aminotriphenylmethane. CARL THOMAE (*J. pr. Chem.*, 1905, [ii], 71, 566–576. Compare Baeyer and Löhr, *Abstr.*, 1890, 1141).—*Benzoyl-p-aminotriphenylmethane*, $C_{26}H_{21}ON$, formed by the action of benzoyl chloride on *p*-aminotriphenylmethane in alcoholic solution or in warm aqueous sodium hydroxide, crystallises in stellate aggregates of needles, melts at 198° , and is only slightly soluble in alcohol, benzene, or glacial acetic acid. When treated with fuming nitric acid in glacial acetic acid solution at 75° , it yields *3-nitro-4-benzoylamino*triphenylmethane, $C_{26}H_{20}O_3N_2$, which crystallises in small, yellow needles, melts at 138° , and is reduced by tin and hydrochloric acid to 2-phenyl-5-diphenylmethylbenzimidazole. *3-Nitro-4-aminotriphenylmethane*, $C_{19}H_{16}O_2N_2$, obtained by hydrolysis of the benzoyl derivative with alcoholic potassium hydroxide, crystallises

in golden leaflets, melts at 98° , is easily soluble in organic solvents, and on addition of concentrated hydrochloric acid to its alcoholic solution gives a dark red coloration, which disappears on dilution with water. 3:4-Diaminotriphenylmethane, $C_{19}H_{18}N_2$, is obtained on reduction of the nitroamino-compound with tin and hydrochloric acid as the *stannochloride*, which crystallises in yellow leaflets or stout needles; the base separates from benzene in crystals containing C_6H_6 and melting at $71-72^{\circ}$; the *hydrochloride* crystallises in long needles. The base gives the following characteristic reactions: with ferric chloride in aqueous solution, a reddish-brown precipitate; with sodium nitrite in cooled acid solution, a yellow precipitate which becomes white, and can be recrystallised from benzene; when fused with benzoic acid at 200° , a yellowish-brown *product*, which in alcoholic-etheral solution has a green fluorescence; with chloranil in alcoholic solution a dark red coloration which is intensified by addition of concentrated hydrochloric acid; with chlorine water in alcoholic solution, a transitory red to green coloration which is more stable if produced by iodine; with bromine in carbon disulphide solution, a red precipitate. The *diacetyl* derivative, $C_{19}H_{16}N_2Ac_2$, forms large, stout crystals, melts at 226° , and is only slightly soluble in ether, benzene, or alcohol. The *dibenzoyl* derivative crystallises from a mixture of alcohol and benzene, melts at 243° , and is oxidised by chromic acid in acetic acid solution to benzamide and *p*-benzoylamino-diphenylquinoylmethane,



which crystallises in golden, glistening, short needles, melts and decomposes at about 163° , and gives a violet coloration with dilute alcoholic potassium hydroxide. *p*-Benzoylamino-diphenyldihydroquinoylmethane, $C_{26}H_{21}O_3N$, formed by reduction of the quinone with sulphur dioxide in aqueous alcoholic solution, crystallises in short, colourless needles, melts and decomposes at about 230° , and reduces boiling ammoniacal silver solution.

Anhydro-3-amino-4-benzoylamino-triphenylmethane [2-phenyl-5-diphenylmethylbenziminazole], $CHPh_2 \cdot C_6H_3 \begin{array}{c} \swarrow NH \\ \searrow N \end{array} CPh$, crystallises from benzene with C_6H_6 , softens at $115-120^{\circ}$, and melts at 205° ; the *stannochloride* crystallises in glistening leaflets or short needles; the *chromate* is yellowish-red; the *platinichloride*, $(C_{26}H_{21}N_2)_2PtCl_6$, forms rhombic plates.

3-Nitro-4-benzoylamino-triphenylcarbinol, $OH \cdot CPh_2 \cdot C_6H_3(NO_2) \cdot NHBz$, formed by oxidation of 3-nitro-4-benzoylamino-triphenylmethane with chromic acid in boiling glacial acetic acid solution, crystallises in long, yellow needles, melts at 169° , and when warmed with alcoholic potassium hydroxide, yields a *product* which crystallises in golden leaflets, melts at 129° , and with concentrated hydrochloric acid in alcoholic solution gives a blood-red coloration which disappears on dilution with water.

G. Y.

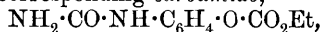
Synthesis of Three Tertiary Dimethylcyclohexanols and the Derived Hydrocarbons. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, 141, 20-22).—The three dimethylcyclohexanols

were prepared by the action of magnesium methyl iodide on the three methylcyclohexanones already described (this vol., i, 275).

1 : 2-Dimethylcyclohexanol, prepared from 2-methylcyclohexanone, is a liquid with a camphoraceous odour, which boils at 166° (corr.), and has a sp. gr. 0.9365 at $0^{\circ}/0^{\circ}$. When treated with zinc chloride in alcohol, it yields the corresponding dimethylcyclohexene, which has a disagreeable odour, boils at 132° (corr.), has a sp. gr. 0.8411 at $0^{\circ}/0^{\circ}$, and is transformed by contact with metallic nickel at 150° (Sabatier and Senderens, Abstr., 1904, i, 156) into dimethylcyclohexane. The latter has a pleasant, camphoraceous odour, boils at 124° (corr.), and has a sp. gr. 0.8002 at $0^{\circ}/0^{\circ}$.

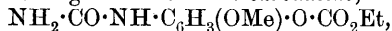
1 : 3-Dimethylcyclohexanol, similarly prepared, resembles its isomeride but is slightly more viscous, boils at 169° (corr.), has a sp. gr. 0.9218 at $0^{\circ}/0^{\circ}$, and yields a crystalline phenylurethane which melts at 93° . The corresponding dimethylcyclohexene boils at 124° and has a sp. gr. 0.8210 at $0^{\circ}/0^{\circ}$, and on hydrogenation, by means of nickel at 150° , yields 1 : 3-methylcyclohexane, a colourless, mobile liquid with a slightly musty odour and a sp. gr. 0.7869 at $0^{\circ}/0^{\circ}$ and boiling at 118° (corr.). 1 : 4-Dimethylcyclohexanol crystallises in long, colourless needles, has a penetrating odour, melts at 50° and boils at 170° (corr.), and yields a crystalline phenylurethane which melts at 103° . The corresponding dimethylcyclohexene boils at 125° (corr.) and has a sp. gr. 0.8208 at $0^{\circ}/0^{\circ}$. 1 : 4-Dimethylcyclohexane is a liquid of pleasant odour, has a sp. gr. 0.7861 at $0^{\circ}/0^{\circ}$, and boils at 119° (corr.). T. A. H.

Aromatic Nitrocarbonic Esters and their Reduction Products. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1905, [iii], 33, 710—712).—Nitrophenyl ethyl carbonate $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO}_2\text{Et}$, prepared by treating phenyl ethyl carbonate, dissolved in acetic acid, with fuming nitric acid, separates from alcohol in pale yellow crystals, and melts at 65 — 66° . On reduction with stannous chloride, it yields the corresponding amino-compound, which is a yellow, syrupy liquid. The acetyl derivative of the amine melts at 118 — 119° , and the corresponding carbamide,



melts at 151 — 152° .

o-Nitromethoxyphenyl ethyl carbonate, similarly prepared, forms yellow crystals and melts at 98 — 99° ; the corresponding amino-compound separates in slightly yellow crystals, melts at 69 — 70° , and yields an acetyl derivative melting at 118° . The carbamide,



melts at 161 — 162° .

T. A. H.

Action of Chloro-formodiethylamide on Nitrophenols and Reduction of the Corresponding Derivatives. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Bull. Soc. chim.*, 1905, [iii], 33, 712—713. Compare Abstr., 1904, i, 559).—When *p*-nitrophenol is warmed with chloro-formodiethylamide, a syrupy nitro-derivative is formed, and this on reduction with stannous chloride in presence of hydrochloric acid yields the corresponding *p*-nitrophenyl diethylcarbamate, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NEt}_2$, which forms large, yellow crystals

and melts at 62° . The *acetyl* derivative melts at $90-91^{\circ}$ and the *carbamide* at $159-160^{\circ}$.

Nitro-o-methoxyphenyl diethylcarbamate, similarly prepared from nitroguaiacol, is crystalline and melts at 83° . The corresponding *amino*-compound is a syrup, but yields a crystalline *acetyl* derivative melting at $122-123^{\circ}$ and a *carbamide* which melts at $170-171^{\circ}$.

T. A. H.

Grignard's Reaction with Dihaloids. CARL A. BISCHOFF (*Ber.*, 1905, **38**, 2078—2083. Compare Grignard and Tissier, *Abstr.*, 1901, i, 316; Ahrens and Stapler, this vol., i, 423).—The interaction of magnesium and ethylene dibromide in ethereal solution is not affected by the presence of a molecular proportion of anisole, but is retarded by addition of a molecular proportion of phenetole, ethyl acetate, or benzil, or by dilution with an excess of ether (from 10 to 70 c.c.) or with benzene. With ethyl acetate, the retardation is the greater the more nearly pure the ester. No reaction takes place even on boiling or on addition of traces of iodine or alcohol, in presence of molecular proportions of acetone, acetophenone, benzophenone, or ethyl oxalate, malonate, or succinate. The reaction takes place slowly in presence of traces of these substances.

The action of the additive compounds formed from 1 mol. of ethylene dibromide, or from 1 mol. of trimethylene dibromide and 1 mol. of magnesium in ethereal solution on 1 mol. of benzil, leads to partial reduction of the benzil to benzoin. On addition of 1 mol. of benzil to the additive compound from 2 mols. of ethylene dibromide with 1 mol. of magnesium, no benzoin is formed, but a *product*, which crystallises in colourless needles and melts at 85° , is obtained.

The action of quinone on the additive compound of ethylene dibromide and magnesium leads to the formation of a green to black mass which is oxidised on exposure to air.

Ethyl succinate does not enter into reaction with magnesium ethylene dibromide.

G. Y.

2- β -Aminoethylphenol and its Methyl Ether. ROBERT PSCHORR and HANS EINBECK (*Ber.*, 1905, i, 2067—2077. Compare Pschorr and Massacin, *Abstr.*, 1904, i, 767).—Contrary to Zwenger's statement (*Annalen*, 1863, **126**, 262), ethyl melilotate cannot be purified by distillation, as it is partially converted into hydrocoumarin.

Melilotylhydrazide, $C_9H_{12}O_2N_2$, formed by the action of hydrazine hydrate in 50 per cent. solution on hydrocoumarin, crystallises from water in colourless leaflets or aggregates of needles, melts at $164-165^{\circ}$, and reduces Fehling's solution when slightly warmed. The *hydrochloride*, $C_9H_{12}O_2N_2 \cdot HCl$, formed along with a small quantity of *s*-dimelilotylhydrazide, by the action of concentrated hydrochloric acid on the hydrazide, crystallises in stellate aggregates of rhombic leaflets and melts at $157-158^{\circ}$.

s-*Dimelilotylhydrazide*, $C_{18}H_{20}O_4N_2$, which is formed by warming melilotylhydrazide with dilute acetic acid, or with evolution of gas, by treating it with sodium nitrite in cold dilute acetic acid solution, crystallises in glistening scales and melts at $176-177^{\circ}$.

The action of sodium nitrite on melilotylhydrazide hydrochloride in aqueous solution under a layer of ether, leads to the formation of the *azoimide*; after evaporation of the ethereal solution, and boiling the residue with alcohol, the impure *azoimide* is obtained as an oil, which partly solidifies in a vacuum, and when distilled under 30—40 mm. pressure yields hydrocoumarin and *s-di-o-hydroxy-β-phenylethylcarbamide*, $\text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$; this crystallises in long leaflets, melts at 187—188°, and distils at 250—280° under 15 mm. pressure. When heated with alcoholic hydrochloric acid in a sealed tube at 150—160° for 4 hours, the carbamide is hydrolysed to *2-β-aminoethylphenol* (*o-hydroxy-β-phenylethylamine*), which is obtained as the *hydrochloride*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot \text{HCl}$, crystallising in stellate aggregates of rhombic leaflets and melting at 152—153°.

o-Hydroxy-β-phenylethyltrimethylammonium iodide, $\text{C}_{11}\text{H}_{18}\text{ONI}$, formed by warming the hydrochloride with sodium and methyl iodide in alcoholic solution, crystallises in prisms, melts at 217—218°, and when distilled with concentrated aqueous sodium hydroxide yields trimethylamine and hydrocoumarone.

Methyl o-methoxyphenylpropionate, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$, formed by the action of methyl sulphate on melilotic acid in aqueous sodium hydroxide solution, is a colourless, highly refractive oil, which boils at 274—275° under 768 mm. pressure, and when boiled with hydrazine hydrate forms the *hydrazide*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_2\text{H}_3$; this crystallises in glistening, colourless, delicate needles and melts at 83—84°. The action of sodium nitrite on the hydrazide in dilute acetic acid solution leads to the formation of *s-di-o-methoxyphenylpropionylhydrazide*, $\text{C}_{20}\text{H}_{24}\text{O}_4\text{N}_2$, which crystallises in long needles, melts at 185—186°, and when heated with methyl alcoholic hydrochloric acid is hydrolysed to hydrazine and methyl *o-methoxyphenylpropionate*. The *hydrochloride* of *o-methoxyphenylpropionylhydrazide*, $\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2 \cdot \text{HCl}$, crystallises in slender, colourless needles, melts at 166—167°, and when treated with sodium nitrite in aqueous solution under ether yields the *azoimide*, which when boiled with absolute alcohol forms *ethyl o-methoxyphenylcarbamate*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$. This is a viscid, colourless oil, which boils at 200° under 19 mm. pressure, and when heated with concentrated aqueous ammonia in a sealed tube at 180° for 5 hours is hydrolysed to *o-methoxy-β-phenylethylamine*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$. This base is an oil which boils at 236—237°, is easily soluble in ether, and absorbs carbon dioxide from the air. The *hydrochloride*, $\text{C}_9\text{H}_{13}\text{ON} \cdot \text{HCl}$, crystallises in long, prismatic plates and melts at 141°; the quaternary *methiodide*, $\text{C}_9\text{H}_{11}\text{ONMe}_3\text{I}$, crystallises in needles and melts at 209°. *o-Methoxystyrene*, $\text{C}_9\text{H}_{10}\text{O}$, formed by heating the quaternary iodide with sodium ethoxide in alcoholic solution at 100° under pressure, is a colourless, mobile liquid, which has a characteristic, intense odour, and boils at 82—83° under 18 mm. pressure (Perkin, Trans., 1881, 39, 411).

o-Methoxybenzaldehyde and magnesium methyl iodide react to form *o-methoxyphenylmethylcarbinol*, $\text{C}_9\text{H}_{12}\text{O}_2$, which is an oil with a pleasant odour, boiling at 124—126° under 17 mm. pressure. When distilled under the atmospheric pressure or when treated with dehydrating

agents, the carbinol forms waxy products which are probably poly-merides of *o*-methoxystyrene. G. Y.

Aromatic Monosubstituted Ethylene Oxides. ERNEST FOURNEAU and MARC TIFFENEAU (*Compt. rend.*, 1905, 140, 1595—1597. Compare this vol., i, 523).—These substances are prepared by submitting the monosubstituted ethylenes suspended in wet ether to the action of iodine and yellow mercuric oxide. The yield in the following cases varies from 50 to 100 per cent. of the theoretical.

Styrene oxide, $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{O} \end{smallmatrix}$.—This is an aromatic liquid which boils at 84—88° under 14—15 mm. and at 188—192° under atmospheric pressure, has a sp. gr. 1·067 at 0° and 1·045 at 24°. When heated with metallic catalytic agents at 200°, it is converted into the isomeric phenylacetaldehyde. Sodium hydrogen sulphite, sulphurous acid, silver nitrate, and mercuric oxide have no action on styrene oxide, and it is also unaffected by boiling dilute sulphuric acid. *Allylbenzene oxide*, $\text{CH}_2\text{Ph} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{O} \end{smallmatrix}$, boils at 94—98° under 15 mm. pressure.

Estragole oxide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{O} \end{smallmatrix}$, boils at 153—156° under 20 mm. pressure, and has a sp. gr. 1·149 at 0°.

Phenylpropylene oxide, $\begin{smallmatrix} \text{CHPh} \\ | \\ \text{CHMe} \end{smallmatrix} > \text{O}$, has a sp. gr. 1·028 at 0°, boils at 90—95° under 15 mm. pressure, and is at the same time partially converted into the isomeric aldehyde. T. A. H.

Condensation of Catechol with Ketones. RUDOLF FABINYI and TIBOR SZÉKY (*Ber.*, 1905, 38, 2307—2312).—The compound $\text{C}_{21}\text{H}_{24}\text{O}_4$, prepared by the condensation of catechol with acetone by heating with glacial acetic acid and hydrochloric acid of sp. gr. 1·19 in a sealed tube at 145°, crystallises from alcohol in needles and melts and decomposes at 314—316°. The action is represented by the equation $2\text{C}_6\text{H}_4(\text{OH})_2 + 3\text{COMe}_2 = \text{C}_{21}\text{H}_{24}\text{O}_4 + 3\text{H}_2\text{O}$. Its *tetracetyl* derivative forms white crystals and melts at 174°; its *tetrabenzoyl* derivative separates from glacial acetic acid in glistening leaflets and melts at 234°. Its *tetrabromo*-derivative, $\text{C}_{21}\text{H}_{20}\text{O}_4\text{Br}_4$, crystallises in needles and melts and decomposes at 130°. Its *tetrabromotetracetyl*-derivative crystallises in tiny leaflets and melts and decomposes at 240°.

When oxidised by nitric acid, the condensation product in question yields the compound $\text{C}_{21}\text{H}_{20}\text{O}_4$, which forms dark red crystals. The tetra-acetyl and tetrabenzoyl derivatives cannot be oxidised in a similar manner, from which it is concluded that the elimination of the four hydrogen atoms takes place from the hydroxyl groups. The tetrabromo-derivative is oxidised to form the compound $\text{C}_{21}\text{H}_{18}\text{O}_4\text{Br}_4$, which separates from nitrobenzene in glistening needles.

The compound $\text{C}_{24}\text{H}_{30}\text{O}_4$, prepared by the condensation of catechol with methyl ethyl ketone, separates from glacial acetic acid in

leaflets and melts at 302—305°. Its *tetracetyl* derivative melts at 165—166°.

The compound $C_{27}H_{36}O_4$, prepared by the condensation of catechol with diethyl ketone, is formed in small yield.

Tentative formulæ are adduced for the condensation products described. A. McK.

Eugenol and Certain of its Derivatives. GEORGE B. FRANKFORDER and MAX LANDO (*J. Amer. Chem. Soc.*, 1905, 27, 641—649. Compare Chasanowitz and Hell, *Abstr.*, 1885, 779).—The purified eugenol used in these experiments had the following physical properties; boiling point, 244·5°; sp. gr., 1·0689 at 20°; n_D , 1·54437; molecular heat of combustion, 1304 cal.; specific heat, 0·5024. The *lithium* and *lead* derivatives of eugenol are described.

By the addition of bromine to a solution of eugenol in chloroform cooled to below 0°, a dark, amorphous mass is obtained. On distilling this product with steam, a residue is obtained consisting of *bromo-eugenol bromide*, $OMe \cdot C_6H_2Br(OH) \cdot CH_2 \cdot CHBrMe$, which forms a nearly white, granular mass; this substance is converted by potassium hydroxide into *bromoeugenol hydroxide*, $C_{10}H_{13}O_3Br$, which forms a white, amorphous powder and melts at 79—82°.

Tribromoeugenol bromide, $C_{10}H_{10}O_3Br_4$, separates from alcohol in large, nearly colourless, triclinic crystals, melts at 118·5°, is soluble in ether, insoluble in water, and is not identical with the tetrabromocompound described by Chasanowitz and Hell (*loc. cit.*). When this substance is warmed with dilute potassium hydroxide, *tribromoeugenol hydroxide*, $C_{10}H_{11}O_3Br_3$, is obtained as a white, amorphous precipitate which is soluble in chloroform and melts at 137°.

When chlorine is led into a solution of eugenol in chloroform, cooled by means of a freezing mixture, a *pentachloro*-compound, $C_{10}H_9O_2Cl_5$, is obtained as a red, crystalline substance; by the action of zinc dust on a solution of this substance in 90 per cent. alcohol, a *zinc* compound, $C_{20}H_{16}O_4Cl_6Zn$, is produced as a white powder. If the pentachlorocompound is treated with potassium hydroxide, *trichloroeugenol hydroxide*, $C_{10}H_{11}O_4Cl_3$, is obtained as an amorphous, brown powder.

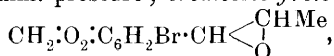
When sulphur dichloride is added to an ethereal solution of eugenol, *thiodieugenol dichloride*, $C_{20}H_{24}O_4S_2Cl_2$, is produced as a bright red precipitate. E. G.

Oxides of Propenylphenol Ethers and their Conversion into the Isomeric Ketones. PAUL HÖRING (*Ber.*, 1905, 38, 2296—2299. Compare Pond and Siegfried, *Abstr.*, 1903, i, 417).—The action of nitric acid on *isosafrole* dibromide in glacial acetic acid solution leads to the formation of *nitro-3:4-methylenedioxy-1-β-bromo-α-acetoxy-n-propylbenzene*, $CH_2 \cdot O_2 \cdot C_6H_2(NO_2) \cdot CH(OAc) \cdot CHBrMe$, which melts at 113°, and is converted by alcoholic potassium hydroxide into *nitroisosafole oxide*, $CH_2 \cdot O_2 \cdot C_6H_2(NO_2) \cdot CH \begin{smallmatrix} \diagup CHMe \\ \diagdown O \end{smallmatrix}$, melting at 113—114°.

In the same manner, when treated with alcoholic potassium hydroxide, the α-acetoxy-β-bromo-derivatives which are formed by the action of sodium acetate on the dibromides of anethole, *isosafrole*, and their

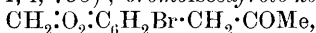
bromo-derivatives, are converted into the corresponding oxides: *anethole oxide*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \text{CHMe} \\ | \\ \text{O} \end{smallmatrix}$, boils at 132° under 11 mm.

pressure; *isosafole oxide*, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \begin{smallmatrix} \text{CHMe} \\ | \\ \text{O} \end{smallmatrix}$, boils at $140\text{--}142^\circ$ under 9 mm. pressure; *bromoisosafole oxide*,



boils at $169\text{--}173^\circ$ under 11 mm. pressure; *dibromoisosafole oxide*, melts at $134\text{--}135^\circ$. These oxides, which are obtained also by the action of alcoholic potassium hydroxide on the β -bromo- α -hydroxy-derivatives which are formed on treating the corresponding dibromides with aqueous acetone, undergo isomeric change into the β -ketones when distilled under the ordinary pressure or when warmed with dilute acids.

Anethole ketone, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{COMe}$, boils at $262\text{--}264^\circ$; *isosafole ketone*, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{COMe}$, boils at $283\text{--}284^\circ$ (compare Wallach, Abstr., 1904, i, 753); *bromoisosafole ketone*,



melts at 103° ; *dibromoisosafole ketone*, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{HBr}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, melts at $116\text{--}117^\circ$. G. Y.

Reduction of Aromatic Amino-acids to the Corresponding Alcohols. ST. LANGGUTH (*Ber.*, 1905, 38, 2062—2064. Compare Herrmann, *Annalen*, 1864, 132, 75; Mettler, this vol., i, 436).—*m*-Aminobenzoic acid is reduced by 4 per cent. sodium amalgam in hot hydrochloric acid solution to *m*-aminobenzyl alcohol, which melts at 97° , and can be distilled without decomposition in a vacuum. When diazotised and coupled with β -naphthol in alkaline solution, *m*-aminobenzyl-alcohol forms *m*-hydroxymethylbenzene-azo- β -naphthol, $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$, which crystallises in purple-red needles and melts at 127° .

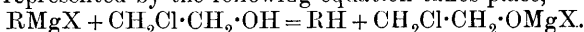
m-Iodobenzyl alcohol, which is formed by the action of potassium iodide and powdered copper on diazotised *m*-aminobenzyl alcohol, is a colourless oil which boils at 154° under 10 mm. pressure.

The action of cuprous cyanide on *m*-aminobenzyl alcohol leads to the formation of *m*-methylolbenzonitrile [*o*-hydroxy-*m*-toluonitrile], $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CN}$, which is a colourless oil; it boils at 165° under 16 mm. pressure, and is converted by aqueous potassium hydroxide into *m*-methylolbenzoic [*o*-hydroxy-*m*-toluic] acid, $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$. This forms a white, crystalline powder, melts at 111° , and boils at 190° under 11 mm. pressure.

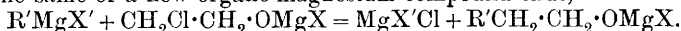
o-Aminobenzyl alcohol may be prepared by the reduction of anthranilic acid with sodium amalgam in hydrochloric acid solution, but only small quantities of *p*-aminobenzyl alcohol are obtained by the reduction of *p*-aminobenzoic acid. G. Y.

Synthesis of Monohydric and Polyhydric Alcohols. VICTOR GRIGNARD (*Compt. rend.*, 1905, 141, 44—46).—The method consists in treating the haloid derivatives of alcohols with mixed organo-

magnesium compounds; thus in the case of glycol chlorohydrin the reaction represented by the following equation takes place,



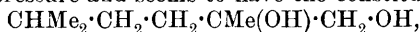
The complex so formed is capable of reacting with a further quantity of the same or a new organo-magnesium compound thus,



The first reaction takes place in the cold and the second while the ether used as solvent is being distilled off. The addition of water to the residue liberates the desired alcohol. From glycol chlorohydrin, phenylethyl alcohol and the following alcohols were prepared by the use of appropriate aromatic organo-magnesium compounds. The yield in each case was about 80 per cent. *o-Tolylethyl alcohol* is an aromatic liquid, boils at 119—120° under 14 mm. and at 237—239° (corr.) under 740 mm. pressure, has a sp. gr. 1.020 at 0° and 1.0095 at 14.8°/4° and n_D 1.53472: the *phenylurethane* melts at 67°. *p-Tolylethyl alcohol* boils at 115—116° under 13 mm. pressure, has a sp. gr. 1.0119 at 0°, 1.0028 at 13°/4°, and n_D 1.52985: the *phenylurethane* melts at 112°. *p-Methoxyphenylethyl alcohol* has an anise-like odour, melts at 24°, boils at 143—144° under 13 mm. pressure, and gives a *phenylurethane* which melts at 123—124°. *α -Naphthylethyl alcohol* melts at 62° and boils at 186° under 17 mm. pressure; the *phenylurethane* melts at 115°.

With glycerol α -monochlorohydrin, magnesium phenyl bromide furnishes a viscous *glycol* which sets to a glassy solid at -60°, boils at 163—165° under 12 mm. pressure, and gives an *acetyl* derivative, which boils at 159—161° under 12 mm. pressure. On oxidation with chromic acid, it yields acetophenone, benzoic acid, and phenylacetic acid, and on distillation at the ordinary temperature undergoes partial dehydration, forming hydratropic acid. This product is probably a mixture of the expected glycol, $CH_2Ph \cdot CH(OH) \cdot CH_2 \cdot OH$, and Tiffeneau's glycol, $OH \cdot CMePh \cdot CH_2 \cdot OH$.

Similarly, when glycerol α -monochlorohydrin is treated with magnesium *isoamyl* bromide a viscous *glycol*, which boils at 128—133° under 12 mm. pressure and seems to have the constitution



is the principal product. It is probable that in this case the complex first formed is $\begin{matrix} CH_2 \\ | \\ O \end{matrix} > CH \cdot CH_2 \cdot OMgBr$, and that this becomes transformed into the ketone, $CH_3 \cdot CO \cdot CH_2 \cdot OMgBr$, which then reacts normally (Abstr., 1903, i, 552).

T. A. H.

A Dihydric Alcohol Related to Phytosterol. TIMOTHÉE KLOBB (*Compt. rend.*, 1905, 140, 1700—1701).—The crystalline substance arnisterol, obtained from *Arnica montana* (Abstr., 1904, i, 410), yields derivatives which indicate that it contains two alcoholic hydroxyl groups. When heated with acetic anhydride at 140—150°, a diacetyl derivative, $C_{28}H_{44}(OAc)_2$, is formed. This is usually obtained in the form of large octahedra (α -acetate) which melt at 181—183°; but sometimes long prisms (β -acetate) are obtained which melt at 100—101° and occasionally an amorphous acetate makes its appearance. In benzene solution (4 grams per 100 c.c.), the α -acetate has a

rotation $[\alpha]_D + 74.2^\circ$, and a molecular weight according to cryoscopic measurements equal to 485 (calculated 498).

A dibenzoyl derivative, $C_{28}H_{44}(OBz)_2$, is obtained from arnisterol by treatment with benzoyl chloride. It melts at 223° and is almost insoluble in cold alcohol. Its molecular weight in benzene solution was found to be equal to 586 (calculated 622).

A phenylurethane, $C_{28}H_{44}(O\cdot CO\cdot NHPh)_2$, is obtained when arnisterol is treated with phenylcarbimide in benzene solution. It can be readily crystallised from boiling ether, and melts and decomposes at about 200° . The molecular weight in acetic acid and ethylene bromide solutions when extrapolated to zero concentration was found to be equal to 624 and 595 respectively (calculated 652). It appears probable that arnisterol is a dihydric alcohol and the name *arnidiol* is proposed for it.

H. M. D.

Action of Potassium Cyanide on Potassium *m*-Nitrobenzenesulphonate. M. HOLLEMAN (*Rec. trav. chim.*, 1905, 24, 194—208).—When potassium *m*-nitrobenzenesulphonate is heated in closed tubes at 180 — 200° with an aqueous solution of potassium cyanide, the following products are formed: potassium *p*-sulphobenzoate, potassium *o*-sulphobenzoate, 2-amino-4-sulphobenzoic acid, 6-amino-2-sulphobenzoic acid, and 4-amino-2-sulphobenzoic acid. When the reaction is allowed to proceed at 100° , resinous products and amines are produced in addition to the potassium salts of *o*- and *p*-sulphobenzoic acids. No azoxy-compounds or hydrazine derivatives are formed in either case. Lobry de Bruyn's explanation of the results obtained by Richter in treating *m*-chloronitrobenzene with potassium cyanide is applicable to these cases (*Abstr.*, 1904, i, 388).

2-Amino-4-sulphobenzoic acid decomposes without melting when gently heated on platinum foil and dissolves in water, giving a blue, fluorescent solution. When diazotised and combined with dimethylaniline, it yields a dye resembling helianthin in colour. 6-Amino-2-sulphobenzoic acid crystallises in agglomerations of slender needles and exhibits reactions similar to those of the foregoing isomeride. 4-Amino-2-sulphobenzoic acid crystallises in fine needles and gives the same reactions as the two foregoing isomerides, but its solution in water is not fluorescent.

The diamide of *p*-sulphobenzoic acid, $NH_2\cdot SO_2\cdot C_6H_4\cdot CO\cdot NH_2$, melts at 230° . The sulphoimide of *o*-sulphobenzoic acid, obtained by the action of phosphorus pentachloride and ammonium carbonate on the acid, melts at 220° .

When 3-nitro-*p*-toluenesulphonic acid or *m*-nitrobenzenesulphonamide is heated with an aqueous solution of potassium cyanide only resinous products are formed. 3-Nitro-*p*-toluenesulphonamide melts at 142.5° (Otto and Gruber give 128° as the melting point).

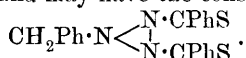
T. A. H.

Action of Thionyl Chloride on Thiobenzamide. LEON TOCHTERMANN (*Bull. Acad. Sci. Cracow*, 1905, 1—2. Compare Michaelis, *Abstr.*, 1893, i, 504, 515).—The action of thionyl chloride

on benzamide leads to the formation of three products, which are separated by fractional crystallisation from benzene.

(1.) *Benzoylthiobenzamide*, $\text{NHBz}\cdot\text{CSPh}$, is a red substance which melts at 117° , is soluble in organic solvents, reacts with phenylhydrazine, and when treated with silver oxide yields dibenzamide.

(2.) A substance which crystallises in long, white needles, melts at $88\text{--}90^\circ$, is indifferent, and may have the constitution



The third product, which was formed in small quantity, could not be purified. G. Y.

Preparation of the Decomposition Products (containing Halogens) from Piperidine. JULIUS VON BRAUN and ADOLPH STEINDORFF (*Ber.*, 1905, **38**, 2336—2339. Compare Abstr., 1904, i, 841, 918, 970, 1019; this vol., i, 206, 341).—An improved method for the preparation of benzoyl- ϵ -chloroamylamide, $\text{NHBz}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\text{Cl}$, from benzoylpiperidine and phosphorus pentachloride, is described. The compound, $2\text{NHBz}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\text{Cl}, \text{CaCl}_2$, formed by allowing fused calcium chloride to remain in contact with an ethereal solution of benzoyl- ϵ -chloroamylamide for some time, forms a white powder which is stable in the air and melts at $148\text{--}149^\circ$.

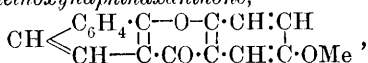
A mixture of benzonitrile and $\alpha\epsilon$ -dibromopentane is formed when benzoylpiperidine is distilled with phosphorus bromide. A method is described by which the benzonitrile may readily be separated from the mixture. A. McK.

Chloromethoxybenzoic Acid. FRITZ ULLMANN and HERMANN KIPPER (*Ber.*, 1905, **38**, 2120—2126. Compare preceding abstract; Ullmann, Abstr., 1903, i, 692; Ullmann and Schlaepfer, Abstr., 1904, i, 570; Goldberg, this vol., i, 59; Ullmann and Lebner, *ibid.*, i, 289).—When heated with piperidine, water, and copper powder under pressure at 160° for 4 hours, or with dimethylamine, water, and copper powder at $135\text{--}140^\circ$ for 5—6 hours, 6-chloro-3-methoxybenzoic acid yields 5-methoxysalicylic acid. Under similar conditions, *o*-chlorobenzoic acid yields salicylic acid.

2-Phenoxy-5-methoxybenzoic acid, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OPh})\cdot\text{CO}_2\text{H}$, is formed by the condensation of phenol and 6-chloro-3-methoxybenzoic acid by means of sodium methoxide and copper. It crystallises in colourless leaflets, melts at 156° , and when warmed with concentrated sulphuric acid yields 2-methoxyxanthone. When warmed with aluminium chloride in xylene solution, this yields methyl chloride and 2-hydroxyxanthone, which crystallises in matted, yellow needles, and melts at 240° (m. p. 231° ; Kostanecki and Rutishauser, Abstr., 1892, 1096).

2- β -Naphthoxy-5-methoxybenzoic acid, $\text{C}_{18}\text{H}_{14}\text{O}_4$, crystallises in stellate aggregates of colourless needles, melts at 160° , dissolves in concentrated sulphuric acid to a colourless solution, which when warmed becomes brown with green fluorescence, and when treated

with phosphorus pentachloride and aluminium chloride in benzene solution yields 2-methoxynaphthaxanthone,

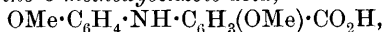


which crystallises in colourless needles, and melts at 256°. With a slightly larger proportion of aluminium chloride and a longer period of heating, the product is 2-hydroxynaphthaxanthone, $\text{C}_{17}\text{H}_{10}\text{O}_3$, which crystallises in brown needles, melts at 287—290°, and dissolves in dilute sodium hydroxide to a yellow solution, or in concentrated sulphuric acid to a yellow solution with green fluorescence. The sodium derivative crystallises in yellow needles.

6-Anilino-3-methoxybenzoic acid, $\text{NHPh} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CO}_2\text{H}$, is obtained by heating aniline and 6-chloro-3-methoxybenzoic acid with a small amount of copper powder, or by boiling aniline, potassium 6-chloro-3-methoxybenzoate, potassium carbonate, and copper powder in amyl alcohol solution in a reflux apparatus. It crystallises in yellow needles, melts at 158°, is readily soluble in alcohol or glacial acetic acid to yellow, or in aqueous alkali hydroxides to colourless solutions, and when heated on the water-bath with concentrated sulphuric acid

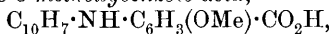
yields 3-methoxyacridone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \\ \text{CO} - \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{OMe} \end{array}$. This crystallises in yellow needles, melts at 282—284°, and dissolves in concentrated sulphuric acid, alcohol, or glacial acetic acid to solutions with green, or in benzene or toluene to solutions with blue fluorescence.

6-o-Methoxyanilino-3-methoxybenzoic acid,



formed from o-anisidine and 6-chloro-3-methoxybenzoic acid, crystallises in glistening, yellow, prismatic needles, melts at 192°, and dissolves in concentrated sulphuric acid to an emerald green solution, which, on warming, becomes brown with green fluorescence.

6-β-Naphthylamino-3-methoxybenzoic acid,



formed from β-naphthylamine and 6-chloro-3-methoxybenzoic acid, crystallises in yellow needles and melts at 171°. G. Y.

Arylsalicylic [Aryloxybenzoic] Acids and their Conversion into Xanthenes. FRITZ ULLMANN and MARGUERITE ZLOKASOFF (*Ber.*, 1905, 38, 2111—2119. Compare *Abstr.*, 1904, i, 417).—Aryloxybenzoic acids are formed by the condensation of potassium o-chlorobenzoate with the potassium derivative of the phenol in presence of copper powder. The aryloxybenzoic acids are mostly converted into the corresponding xanthenes by the action of concentrated sulphuric acid.

o-Tolyloxybenzoic acid, $\text{C}_7\text{H}_7 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, crystallises in colourless needles, melts at 133·5°, and is easily soluble in alcohol, ether, or benzene. 4-Methylxanthone, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} - \text{C} \cdot \text{Me} \cdot \text{CH} \\ \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{CH} \end{array}$, crystallises in white needles, melts at 126° (m. p. 105°; Schoepff, *Abstr.*, 1893, 217), and dissolves in concentrated sulphuric acid to a yellow solution with green fluorescence.

m-Tolyloxybenzoic acid crystallises in needles, melts at 95° , and forms 1-(or 3-)methylxanthone, which crystallises in large, stellate aggregates of leaflets, and melts at $89-91^{\circ}$. Weber's 3-methylxanthone (Abstr., 1892, 1092; compare Strobach, Abstr., 1902, i, 171) was probably 3:5-dimethylxanthone.

p-Tolyloxybenzoic acid forms large crystals, melts at 118.5° , and yields 2-methylxanthone, which crystallises in large needles, melts at 121° (m. p. 105° ; Graebe and Feer, Abstr., 1887, 152), and dissolves in concentrated sulphuric acid to a yellow solution with green fluorescence.

1:3:4-*Xylyloxybenzoic acid* crystallises in almost colourless needles, melts at 152° , dissolves readily in alcohol, ether, or boiling benzene, and forms 2:4-dimethylxanthone, $C_{15}H_{12}O_2$, which crystallises in large, glistening, transparent leaflets, melts at 152° , and dissolves in concentrated sulphuric acid to an intensely yellow solution, with green fluorescence.

β -*Naphthylloxybenzoic acid* crystallises in white needles, melts at 124° , and dissolves in concentrated sulphuric acid to a colourless solution, which when warmed becomes brownish-yellow with a green fluorescence, the β -naphthoxy-acid forming β -phenonaphthaxanthone in a 20 per cent. yield, the remainder being apparently sulphonated. Better yields of β -phenonaphthaxanthone (Kostanecki, Abstr., 1892, 1099) are obtained by heating the β -naphthoxy-acid in benzene solution with phosphorus pentachloride and with aluminium chloride successively.

Salicylic acid o-methoxyphenyl ether forms small, almost colourless, glistening crystals, melts at 112° , and, when heated in benzene solution with phosphorus pentachloride and with aluminium chloride successively, yields 4-hydroxyxanthone, melting at 241° (m. p. 224° , Kostanecki and Rutishauser, Abstr., 1892, 1096), and 4-methoxyxanthone, melting at 173° (m. p. 165° , Dreher and Kostanecki, Abstr., 1893, i, 1, 217).

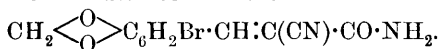
2-Methoxyxanthone is formed by the action of concentrated sulphuric acid on the *p*-methoxyphenyl ether of salicylic acid, obtained by the condensation of *o*-chlorobenzoic acid with the monomethyl ether of quinol. G. Y.

Action of Bromine on certain Non-saturated Compounds. GALEAZZO PICCININI (*Atti R. Accad. Torino*, 1904—1905, 40, 463—486).—Many unsaturated compounds are known which are stable towards bromine, and in these the carbon atoms connected by the double linking are generally attached to energetic electro-negative groups; the double linking itself confers a negative character on the carbon atoms on either side.

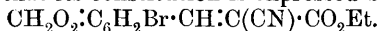
The author has investigated the action of bromine on certain unsaturated aromatic cyano-amides. He finds that the melting points of the bromo-derivatives prepared are higher than those of the amides themselves by an approximately constant amount. Also, ethyl bromomethylenedioxyphenyl- α -cyanoacrylate and ethyl bromodimethoxyphenyl- α -cyanoacrylate have melting points practically identical with those of the bromo-aldehydes to which they give rise on decomposition. Further, halogenated aromatic derivatives are decomposed by aqueous or alcoholic solutions of potassium hydroxide if the halogen is in the

side chain, whilst, if the halogen is in the benzene nucleus, reaction only takes place if it is near a nitro-group.

α -Cyano- β -piperonylideneacetamide melts at 212—213°, and not at 209° as previously stated (Abstr., 1904, i, 91); it is best prepared by condensing piperonaldehyde and cyanoacetamide in presence of glacial acetic acid or 15 per cent. aqueous ammonia. Its bromo-derivative, melting at 245° (*loc. cit.*), yields bromopiperonaldehyde when distilled with sodium hydroxide in a current of steam, so that the bromine atom must be in the benzene nucleus, the constitution being



Bechert (Abstr., 1894, i, 489) has erroneously ascribed to a bromo-derivative, obtained from ethyl methylenedioxyphenyl- α -cyanoacrylate, and melting at 131°, the formula $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CBr} : \text{C}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$; the author shows that its constitution is expressed by



p-Hydroxy-*m*-methoxyphenyl- α -cyanoacrylamide yields a bromo-derivative, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}(\text{OMe}) \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$, which crystallises from alcohol in small, yellow leaflets melting and decomposing at 234—235°, and dissolves in acetic acid. On oxidation with chromic acid, it yields bromovanillin.

Dihydroxyphenyl- α -cyanoacrylamide yields a bromo-derivative, $\text{C}_6\text{H}_2\text{Br}(\text{OH})_2 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$, which blackens at 230—235°, melts and decomposes at about 260°, and dissolves in dilute potassium hydroxide solution, giving a carmine solution turning yellow on boiling.

Ethyl 3:4-dimethoxyphenyl- α -cyanoacrylate yields a bromo-derivative, $\text{C}_6\text{H}_2\text{Br}(\text{OMe})_2 \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, which crystallises from 90 per cent. alcohol in shining, pale yellow leaflets, melting at 154°, and is soluble in benzene, acetone, or boiling alkali solutions. When boiled with 10 per cent. sodium hydroxide solution, it is partially decomposed, yielding bromoveratraldehyde, $\text{C}_6\text{H}_3\text{Br}(\text{OMe})_2 \cdot \text{CHO}$, which can also be obtained by direct bromination of veratraldehyde, and crystallises from water in slender, colourless needles, melting at 151°; it gives a yellow, crystalline phenylhydrazone, reduces ammoniacal silver nitrate solution, and has the normal molecular weight in freezing benzene.

The bromo-derivative of ethyl cinnamenyl- α -cyanoacrylate, $\text{CHPhBr} \cdot \text{CHBr} \cdot \text{CH} : \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$, melts at 100°, and not at 95° as stated by Bechert (*loc. cit.*); it has the normal molecular weight in freezing benzene, and when oxidised by means of chromic acid yields $\alpha\beta$ -dibromo- β -phenylpropionic acid.

T. H. P.

Hydrophthalic Acids: Two New Hydrophthalic Anhydrides

I. GINO ABATI and LUIGI DE BERNARDINIS (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1905, [iii], 11, 61—70).—The reduction of sodium phthalate by sodium amalgam when heated yields the following two anhydrides:

cis- Δ^3 -Tetrahydrophthalic anhydride, $\text{C}_6\text{H}_8 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{O}$, which crystallises from water in shining, white scales, melting at 70°, and is readily soluble in alcohol or sodium carbonate solution; it has an acid reaction

towards litmus paper, and can be titrated with standard alcoholic potassium hydroxide solution; by heating at 220—230°, it is transformed into Δ^1 -tetrahydrophthalic anhydride; when neutralised with sodium hydroxide, it is oxidised by permanganate, although less slowly than the tetrahydrophthalic acids. It gives a *dibromo*-derivative, $C_8H_{10}O_4Br_2$, which separates from aqueous alcohol in whitish crystals melting at 187°, and slowly reduces permanganate solution. With *p*-anisidine, it gives a *compound*, $C_6H_8 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot C_6H_4 \cdot OMe$, which crystallises from alcohol in white leaflets, melting at 88°.

$\Delta^{1:3}$ -*Dihydrophthalic anhydride*, $C_6H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$, crystallises from alcohol in shining, white scales melting at 58°, and is readily soluble in ether or benzene, and slightly so in water; it has an acid reaction towards litmus paper, and dissolves readily in sodium carbonate solution; when heated at about 225°, it is transformed into another anhydride, which could not be purified, but on treatment with *p*-anisidine in alcoholic solution yields an imide melting at 89°; it is not acted on by bromine or hydrobromic acid.

Besides the above anhydrides, the reduction of sodium phthalate by sodium amalgam gives a small quantity of a *substance* which melts at 174° and is probably a hydrophthalic acid; on boiling with acetic anhydride, it yields a crystalline product melting at 97—98°.

T. H. P.

Synthesis of α -Amino-acids by means of Ethyl Phthaliminomalonate. S. P. L. SÖRENSEN (*Zeit. physiol. Chem.*, 1905, 44, 448—460. Compare Abstr., 1903, i, 833).—Various α -amino-acids have been synthesised by the action of different haloid derivatives on the sodio-derivative of ethyl phthaliminomalonate and subsequent hydrolysis with baryta and then with hydrochloric acid. Phenylalanine has been obtained from benzyl chloride, allylglycine from allyl iodide; ornithine from γ -bromopropylphthalimide (Abstr., 1888, 1292); α -aminoadipic acid from γ -chlorobutyronitrile (Abstr., 1890, 1221); $\alpha\epsilon$ -diaminopimelic acid from trimethylene bromide; $\alpha\delta$ -diamino-adipic acid from ethylene bromide, and α -amino- δ -hydroxyvaleric acid by using a large excess of trimethylene bromide.

Full directions for the preparation of ethyl sodiophthaliminomalonate are given. Good yields of the synthetical products are only obtained when the condensation proceeds in the absence of alcohol, and it is essential that all the reagents should be free from water. J. J. S.

Synthesis of Aldehydes by means of Formic Acid. JOSEF HOUBEN (*Chem. Zeit.*, 1905, 29, 667).—The author claims priority for his work over that of Zelinski on the same subject (*ibid.*, 1904, 28, 303). As the result of a number of experiments, the following conditions were found to give the best yield of phenylacetaldehyde. A solution of 60 grams of benzyl chloride in 200 c.c. of ether, after treatment with 11.5 grams of magnesium, was slowly run into 10.9 grams of glacial formic acid dissolved in 100 c.c. of ether, the mixture being kept thoroughly shaken and cooled. After standing for 36 hours,

it was decomposed with ice and dilute sulphuric acid; the ethereal extract from this solution was shaken with sodium hydrogen sulphite, and the resulting compound, after decomposition with sodium carbonate and extraction with ether, yielded 5.3 grams of phenylacetaldehyde boiling at 204—209°. P. H.

Decahydro- β -naphthyl Ketone and Decahydro- β -naphthylamine. HENRI LEROUX (*Compt. rend.*, 1905, 141, 46—47).—*Decahydro- β -naphthyl ketone*, $C_{10}H_{16}O$, prepared by oxidising decahydro- β -naphthol (this vol., i, 278) with chromic acid, is a colourless liquid with a strong, unpleasant odour; it boils at 116° under 15 mm. pressure, has a sp. gr. 0.988 at 0° and 0.979 at 16°, n_D 1.4834 at 16°, and is slightly soluble in water, readily so in alcohol and ether. The *sodium hydrogen sulphite* derivative crystallises from water in nacreous lamellæ. The *semicarbazone* separates from alcohol in slender needles and melts at 195°; the *phenylhydrazone* rapidly becomes coloured on exposure to air; the *oxime* forms small, colourless prisms and melts at 76° and on reduction with sodium and alcohol forms *decahydro- β -naphthylamine*, $C_{10}H_{17}\cdot NH_2$. This is a colourless liquid with an unpleasant odour, it distils at 112° under 15 mm. pressure, and is a strong base absorbing carbon dioxide from the air. The *hydrochloride* forms small, colourless prisms, and the *picrate* is crystalline and melts at 203—204°. T. A. H.

Action of a Mixture of Glacial Acetic Acid and Hydriodic Acid on Quinones. KASIMIR LAGODZINSKI (*Ber.*, 1905, 38, 2301—2306. Compare Liebermann and Mamlock, this vol., i, 531).—When hydriodic acid of sp. gr. 1.70 is added to a boiling mixture of anthraquinone and glacial acetic acid, the anthraquinone dissolves and from the brown solution brown, glistening needles separate on cooling. When this *compound*, the constitution of which has not been determined, is warmed, iodine separates, the residue consisting of anthranol which melts at 154°; a similar change takes place when the solution of the compound in ether, benzene, or alcohol is heated. A mixture of glacial acetic acid and hydriodic acid appears to attack anthranol itself.

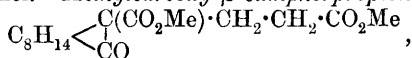
By the action of a mixture of glacial acetic acid and hydriodic acid on alizarin, red, glistening needles of a *compound* were obtained, whilst by the action on phenanthraquinone dark brown crystals of a *compound* separated. A. McK.

Camphoracetic and β -Camphorpropionic Acids. ALBIN HALLER (*Compt. rend.*, 1905, 141, 13—16. Compare this vol., i, 533).

—*Methyl carboxycamphoracetate*, $C_8H_{14}\begin{matrix} C(CO_2Me) \cdot CH_2 \cdot CO_2Me \\ \diagup \\ CO \end{matrix}$, prepared by the action of methyl iodoacetate on methyl camphorcarboxylate in presence of sodium methoxide, is a yellow oil which boils at 194—196° under 15 mm. pressure, does not solidify above 0°, has $[\alpha]_D + 65.42'$ in alcohol, and is soluble in organic solvents but insoluble in water. When heated with potassium hydroxide in alcohol, it yields potassium camphoracetate, potassium carbonate, and methyl

alcohol, and with sodium ethoxide in alcohol, a viscous, uncrystallisable acid from which no homocamphoric acid could be isolated.

Camphoracetic acid, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \\ \text{CO} \end{smallmatrix}$, crystallises from boiling water in colourless, flattened needles, melts at 175° , and has $[\alpha]_D + 70^\circ 42'$ in alcohol. *Methylcarboxy- β -camphorpropionate*,



prepared from methyl camphorcarboxylate and methyl β -iodopropionate, is a thick, yellow oil which boils at $200\text{--}204^\circ$ under 10 mm. pressure, has $[\alpha]_D + 51^\circ 22'$, and is insoluble in water and alkalis but dissolves in most organic solvents. When hydrolysed with potassium hydroxide in alcohol or with dilute (10 per cent.) sulphuric acid, it

yields *β -camphorpropionic acid*, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \\ \text{CO} \end{smallmatrix}$. This is

purified through the lead salt and then melts at $52\text{--}53^\circ$, has $[\alpha]_D + 45^\circ 35'$ in alcohol, and is readily soluble in alcohol or ether, and slightly so in water. These and previous results indicate that methyl camphorcarboxylate, unlike the sodium derivative of cyanocamphor, always behaves as a β -ketone towards alkyl iodides or iodo-esters.

T. A. H.

Alkylthujones and Compounds of Thujone (Tanacetone) with Aldehydes. ALBIN HALLER (*Compt. rend.*, 1905, 140, 1626—1631. Compare Abstr., 1904, i, 600, and this vol., i, 214, and Semmler, Abstr., 1904, i, 176).—The alkylthujones were prepared by adding the appropriate alkyl iodide to a mixture of thujone and dry ether in which the requisite quantity of sodamide had been dissolved previously. The products are mobile liquids having odours resembling

that of thujone. *Methylthujone*, $C_8H_{14} \begin{smallmatrix} \text{CHMe} \\ | \\ \text{CO} \end{smallmatrix}$, boils at 90° under

16 mm. pressure and has $[\alpha]_D 16^\circ 16'$ at 15° , and a sp. gr. 0.9102 at $15^\circ/4^\circ$; the *semicarbazone* crystallises from alcohol, melts at 164° , and re-melts at $183\text{--}184^\circ$. A small quantity of *dimethylthujone* is also formed. *Ethylthujone* distils at $93\text{--}96^\circ$ under 13 mm. pressure, has $[\alpha]_D - 48^\circ 23'$ at 15° , and a sp. gr. 0.9155 at $15^\circ/4^\circ$ and yields a *semicarbazone*, which crystallises in small needles, melts at 131° , and re-melts at 171° . *Propylthujone* boils at $107\text{--}110^\circ$ under 16 mm. pressure, has $[\alpha]_D - 48^\circ 28'$ at 15° , and a sp. gr. 0.9102 at $15^\circ/4^\circ$; the *semicarbazone* resembles that of ethylthujone and melts at $164\text{--}168^\circ$. *Allylthujone* distils between 108° and 110° under 15 mm. pressure, has $[\alpha]_D - 50^\circ 47'$ at 15° , and a sp. gr. 0.9254 at $15^\circ/4^\circ$, and furnishes a *semicarbazone*, which crystallises in needles, melts at $130\text{--}131^\circ$, and re-melts at $150\text{--}151^\circ$. It was observed that by the action of sodamide on thujone alone a reduction in the value of the rotatory power was produced, consequently no deductions as to the effect of the introduction of alkyl groups on the value of the rotatory power can be deduced from the specific rotations now recorded.

Benzylidenethujone, prepared by Semmler's process (Abstr., 1904, i, 176), has $[\alpha]_D - 590^\circ 8'$ in alcohol at 15° . *Anisylidenethujone*,

$C_8H_{14} \begin{matrix} & C:CH \cdot C_6H_4 \cdot OMe \\ & \diagup \quad \diagdown \\ & CO \end{matrix}$, crystallises in small, white needles, melts at 85° , boils at $223-224^\circ$ under 14 mm. pressure, and has $[\alpha]_D - 829.3'$ in alcohol at 15° . *Piperonylideneethujone* crystallises in small, white scales which become yellow on exposure to light, melts at 114° , and has $[\alpha]_D - 765^\circ$ in alcohol at 15° . The high specific rotations of these substances afford further evidence of the influence of ethylenic linkings in increasing the values of this constant (compare Abstr., 1903, ii, 622).

Piperonylideneisothujone, similarly prepared from *isothujone*, crystallises in faintly yellow, flattened needles, melts at $131-132^\circ$, and is optically inactive. T. A. H.

Terpinene Nitrosite. T. AMENOMIYA (*Ber.*, 1905, 38, 2020—2021).—When nitric acid of sp. gr. 1.4 is warmed with a solution of terpinene nitrite in glacial acetic acid and the product poured into water, yellow crystals of the compound $C_{10}H_{15}O_6N_3$, melting at about 73° , are formed. By the action of aniline on it, the compound $C_{16}H_{21}O_4N_3$ is formed and separates from alcohol in yellow needles, melting at 145° . The reaction probably proceeds according to the equation $C_{10}H_{15}O_6N_3 + C_6H_7N = C_{16}H_{21}O_4N_3 + HNO_2$. A. McK.

Ginger Grass Oil. HEINRICH WALBAUM and O. HÜTHIG (*J. pr. Chem.*, 1905, [ii], 71, 459—473. Compare this vol., i, 53; Gildemeister and Stephan, Abstr., 1897, i, 81; Schimmel & Co., Abstr., 1904, i, 603; this vol., i, 536).—The constants for commercial ginger grass oil lie within the following limits: sp. gr. $0.9277-0.9458$ at 15° ; $\alpha_D - 29^\circ 25' + 22^\circ 40'$; saponification number $0.9-3.2$; saponification number after acetylation $130-172$; ester number $9.5-24$. The oil boils at $50-100^\circ$ under 5.6 mm. pressure; the lowest boiling fractions contain *d*- α -phellandrene, dipentene, and *d*-limonene; the fractions boiling at $80-90^\circ$ contain an aldehyde, $C_{10}H_{16}O$, which is isolated as the sodium hydrogen sulphite compound; the fraction boiling at $80-83.5^\circ$ contains also *i*-carvone; whilst geraniol and dihydrocuminol are found principally in the fractions boiling at $85-95^\circ$.

The aldehyde, $C_{10}H_{16}O$, occurs in the ginger grass oil to the extent of about 0.2 per cent.; it is a colourless oil, with an odour resembling that of heptaldehyde or of citronellal, boils at $76-78^\circ$ under 5 mm., or at $221-224^\circ$ under 754 mm. pressure, has a sp. gr. 0.9351 at 15° , $\alpha_D \pm 0^\circ$, and $n_D 1.47348$ at 20° . The semicarbazone, $C_{11}H_{19}ON_3$, melts at $169-170^\circ$; the oxime melts at $115-116^\circ$; the phenylhydrazone melts at 63° ; the semioxamazone melts at $244-245^\circ$; the derivative with naphthacinchonic acid melts at 261° . The aldehyde is slowly oxidised on exposure to the air, more quickly by treatment with silver oxide, to the acid $C_{10}H_{16}O_2$, which crystallises in leaflets, melts at $106-107^\circ$, boils at $133-135^\circ$ under 4 mm. pressure, and when treated with bromine in chloroform solution forms a dibromide, $C_{10}H_{16}O_2Br_2$; this crystallises in glistening leaflets and melts at $116-117^\circ$. The same acid is obtained on acidification of the product of alkaline hydrolysis from ginger grass oil. The acetate, obtained by reducing the aldehyde with zinc dust and glacial acetic acid, is a liquid with a fruity odour; it boils at $98-102^\circ$ under 4 mm. pressure,

and on hydrolysis yields the *alcohol* $C_{10}H_{18}O$, which is a viscid oil having a pleasant odour. It boils at $89-91^{\circ}$ under 4 mm., or at $236-238^{\circ}$ under 755 mm. pressure, has a sp. gr. 0.9419 at 15° , $\alpha_D \pm 0^{\circ}$, and n_D 1.48652 at 22° . The *phenylurethane*, formed by the action of phenylcarbimide on the alcohol, melts at $100-101^{\circ}$; the *diphenylurethane*, formed by the action of diphenylcarbamic chloride and pyridine on the alcohol, melts at $84-86^{\circ}$.

Geraniol and dihydrocuminol are separated partially by treatment with calcium chloride or with phthalic anhydride, as dihydrocuminol does not combine with either of these reagents; on the treatment of the impure dihydrocuminol with 90 per cent. formic acid, the remainder of the geraniol is converted into terpene or polyterpenes, whilst only a small fraction of the dihydrocuminol is converted into *p*-cymene. A lævorotatory ginger grass oil yielded dihydrocuminol which boils at $92-93.5^{\circ}$ under 5 mm., or at $226-227^{\circ}$ under 767 mm. pressure, and has a sp. gr. 0.9510 at 15° , $\alpha_D - 13^{\circ}18'$, and n_D 1.49629 at 20° .

The *p*-cymene formed from dihydrocuminol boils at $175-176^{\circ}$, and has a sp. gr. 0.8608 at 15° , $\alpha_D + 0.4^{\circ}$, and n_D 1.48935 at 20° . When dihydrocuminol is heated with zinc chloride or pyruvic acid, in addition to *p*-cymene, there is obtained a *product* which has an odour resembling that of pinol, boils at $185-200^{\circ}$, and forms a crystalline *additive* product with iodine melting at $169-170^{\circ}$.

Oxidation of dihydrocuminol with 4 per cent. potassium permanganate solution leads to the formation of terephthalic and *p*-hydroxy-isopropylbenzoic acids, but with 1 per cent. solution, to the formation of a *glycol* which could not be crystallised.

Dihydrocuminolaldehyde, $C_{10}H_{14}O$, boils at 85° under 4 mm., or at 235° under 755 mm. pressure, and has a sp. gr. 0.9698 at 15° , $\alpha_D - 37^{\circ}54'$, and n_D 1.50702 at 20° . The *semicarbazone* melts at $198-198.5^{\circ}$; the *semioxamazone* melts at 228° .

Dihydrocuminic acid, formed from dihydrocuminol, crystallises in leaflets and melts at $130-131^{\circ}$, but is not identical with Baeyer and Villiger's acid obtained from nopic acid (Abstr., 1896, i, 622), as it forms a *hydrobromide* melting at 175° . This is isomeric, and not identical with Baeyer and Villiger's bromotetrahydrocuminic acid (*loc. cit.*).

On acetylation of dihydrocuminol with acetic anhydride and distillation of the product, there was obtained a fraction containing 97.71 per cent. of the *acetate*, $C_{10}H_{16}O.Ac$; this boiled at $90-91^{\circ}$ under 4 mm. pressure, and had a sp. gr. 0.9725 at 15° , $\alpha_D - 4^{\circ}30'$, n_D 1.47615 at 20° , and an ester number 282.

Reduction of dihydrocuminol with sodium in amyl alcoholic solution leads to the formation of *tetrahydrocuminol* which boils at $79-80^{\circ}$ under 5 mm. or at $216-218^{\circ}$ under the ordinary pressure, has a sp. gr. 0.9419 at 15° , and forms a *phenylurethane*, $C_{17}H_{23}O_2N$, melting at $85-86^{\circ}$.
G. Y.

Pyrogenetic Decomposition of Lac Resin. ALEXANDER ÉTARD and E. WALLÉE (*Compt. rend.*, 1905, 140, 1603—1606).—When lac resin is submitted to destructive distillation, it furnishes 22 per cent. of a light "coke" apparently derived from starchy matter, 6 per cent. of

gas, 52 per cent. of a yellow oil, and 20 per cent. of an aqueous distillate. The oil contains, in addition to oleic acid and small quantities of hexoic and sebacic acids, the following neutral substances: a terpene, apparently of the dipentene group, boiling at 170—175°; a terpenic hydrocarbon which is greenish-blue in colour and boils at 235—240°; a paraffin, $C_{32}H_{66}$, which crystallises in colourless spangles, melts at 61—62°, boils at 360°, and resembles the hydrocarbons found in association with chlorophyll; and a polyterpene which boils at 310°. These results indicate that lac resin may be composed of a series of unstable oleates of polyterpenes.

T. A. H.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1905, **38**, 2166—2168. Compare *Abstr.*, 1903, i, 270, 713; 1904, i, 81, 908; Gilbody and Perkin, *Trans.*, 1902, **81**, 1040).—Trimethylbrazilone, when heated on the water-bath with an excess of phenylhydrazine and glacial acetic acid, yields a *phenylhydrazine* derivative, $C_{22}H_{18}ON_2(OMe)_3$. It crystallises from ethyl acetate in slender, yellow needles, melts at 239—242°, and cannot be acetylated. At higher temperatures, the product is Gilbody and Perkin's deoxy-trimethylbrazilone, which melts at 165—168° and not at 173°.

No corresponding nitrogen derivative has so far been obtained from tetramethylhæmatoxolone. When this compound is heated on the water-bath with glacial acetic acid and phenylhydrazine, the product is *deoxytetramethylhæmatoxolone*, $C_{16}H_{18}O(OMe)_4$. It crystallises from benzene in colourless needles and melts at 170—175°.

J. J. S.

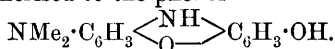
Oxonium and Ammonium Salts. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 2143—2154).—Electrical conductivity determinations of dimethylpyrone hydrochloride and sulphate indicate that these salts are practically completely hydrolysed in aqueous solution. The values for solutions of the salts are smaller than the conductivity values for solutions of the free acid of equivalent strength, especially in the case of concentrated solutions of the sulphate. This is not attributed to the presence of definite amounts of pyronium salt in the solution, since sucrose, chloral hydrate, and dextrose produce a similar lowering on the conductivity of solutions of hydrochloric and sulphuric acids.

Oxonium salts of the type $C_6H_4 \begin{smallmatrix} \text{R} \\ \text{O} \end{smallmatrix} \text{X} C_6H_4$ or $C_6H_4 \begin{smallmatrix} \text{R} \\ | \\ \text{O} \end{smallmatrix} \text{X} C_6H_4$

are somewhat more stable but are also readily decomposed by water. The tendency of quadrivalent oxygen to form salts and bases is thus extremely small compared with the same tendency of quinquevalent nitrogen. Attempts have been made to distinguish between Bernthsen's ammonium, $NH_2Cl \cdot C_6H_3 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} C_6H_4$, and Kehrman's

thionium formula, $NH_2 \cdot C_6H_3 \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} Cl C_6H_4$, for thiazine dyes and corresponding oxazine salts (*Abstr.*, 1902, i, 566). Kehrman's observations on the readiness with which the bases can be diazotised are not regarded as incompatible with the ammonium formula. All these salts are much more stable than the oxonium salts, but no conductivity determinations could be made on account of the fact that they are so sparingly soluble. As examples of soluble aminophenaz-

thionium salts, methylene-blue and Lauth's-violet, and of soluble aminophenoxazonium salts, Meldola's blue, have been selected. The results of conductivity determinations show that the salts are not hydrolysed to any appreciable extent, in fact to about the same extent as ammonium or potassium chloride, and the values obtained, especially with Meldola's blue, correspond closely with those previously given for pararosanilinium chloride (Hantzsch and Osswald, Abstr., 1900, i, 256). The conductivities of solutions obtained by mixing the above salts with equivalent amounts of sodium hydroxide have been determined. With Meldola's blue, the colour is almost instantaneously destroyed and the value for the conductivity is practically that of pure sodium chloride of equivalent concentration, thus indicating that the ammonium base is instantaneously isomerised to the phenol



The base from Lauth's-violet is somewhat more stable, and the value of the conductivity falls to that of sodium chloride only after some 28 hours. The methylene-blue base, on the other hand, is perfectly stable; the conductivity of the solution obtained on the addition of an equivalent of alkali to its salts remains constant, $\nu = 256$, μ for ammonium base = 148, since the ammonium base cannot undergo intramolecular rearrangement.

The conclusion is drawn that on the whole the facts are more in harmony with the ammonium than with the oxonium and thionium formulæ for the oxazine and thiazine dyes, since it is difficult to see why the introduction of amino-groups into an extremely unstable oxonium or thionium salt should render it as stable and as little hydrolysed as ammonium chloride. Similar arguments are used with reference to carbonium salts, and in reply to Baeyer (this vol., i, 281) it is pointed out that the coloured sulphate from colourless *p*-trihalogen triphenylcarbinol may have an ortho-quinonoid structure although a para-quinonoid formula is impossible. J. J. S.

Fisetin Derivatives containing less Oxygen. J. BERSTEIN, C. FRASCHINA and STANISLAUS VON KOSTANECKI (*Ber.*, 1905, **38**, 2177—2182).—2'-Hydroxy-3:4-dimethoxychalkone, prepared by condensing veratraldehyde with *o*-hydroxyacetophenone, crystallises from alcohol in orange-yellow plates melting at 115°. The alcoholic solution, when heated with hydrochloric acid, is converted into 3':4'-dimethoxyflavanone, which crystallises in colourless plates melting at 123—125°, dissolves in alcoholic sodium hydroxide with an orange yellow, and in sulphuric acid with an orange-red, coloration. 3-Bromo-3':4'-dimethoxyflavanone, prepared by bromination in disulphide solution, forms colourless prisms which melt and decompose at 160°. 3':4'-Dimethoxyflavone, formed by the action of concentrated potassium hydroxide on the preceding compound, separates from alcohol in colourless needles melting at 154—155°; it dissolves in sulphuric acid with a yellow coloration, and the dilute alcoholic solution has an intensely violet fluorescence.

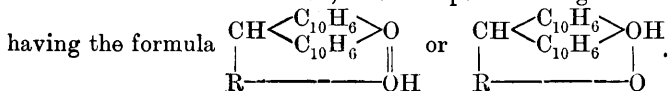
3'-4'-Dihydroxyflavone crystallises in bright yellow prisms melting at 243°; it dyes cotton yarn bright yellow with aluminium mordants and

grey to black with iron mordants. 3':4'-*Diacetoxyflavone*, $C_{15}H_8O_2(OAc)_2$, crystallises in colourless, glistening needles melting at 171° . 3-*Isonitroso*-3':4'-*dimethoxyflavanone*, prepared by the action of amyl nitrite and hydrogen chloride on the dimethoxyflavanone, crystallises from benzene in colourless rosettes of needles; it gives orange-yellow shades with cobalt mordants.

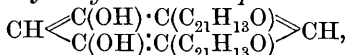
3':4'-*Dimethoxyflavonol* crystallises in large, yellow needles, melts at $199-200^\circ$, and gives an intense yellow coloration with sulphuric acid; it forms a sparingly soluble yellow sodium salt. *Acetyl*-3':4'-*dimethoxyflavonol*, $OAc \cdot C_{15}H_7O_2(OMe)_2$, separates from dilute alcohol in long, colourless needles melting at $130-131^\circ$. 3':4'-*Dihydroxyflavonol* results from the action of hydrogen iodide on the foregoing; it crystallises in short, broad, yellow needles melting and decomposing at 303° , gives a yellowish-red coloration with sodium hydroxide, and dyes orange-yellow with aluminium and grey to black with iron mordants. *Acetyl*-3':4'-*diacetoxyflavonol* forms colourless needles melting at $199-200^\circ$. The whole of the 14 hydroxy-derivatives of flavone have now been described.

E. F. A.

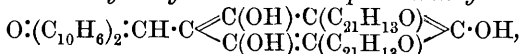
Pyranic [Xanthyl] Phenols. ROBERT FOSSE and A. ROBYN (*Compt. rend.*, 1905, 140, 1538—1540. Compare Abstr., 1904, i, 83, 336).—The dinaphthaxanthyl phenols already described are insoluble in aqueous, but soluble in alcoholic, alkali hydroxides. This anomalous behaviour of the hydroxyl group is probably due to an intermolecular neutralisation, the compound being an oxygen salt



In the present paper, the condensation products of dinaphthaxanthonium salts with resorcinol, pyrogallol, and *m*-diethylaminophenol are described. 1:3-*Dihydroxy*-4:6-bis(dinaphthaxanthyl) benzene,



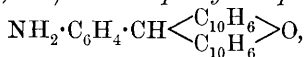
obtained from dinaphthaxanthonium bromide and resorcinol, crystallises from ethyl acetate, decomposes without melting, and is insoluble in aqueous, but soluble in alcoholic, alkali hydroxides; the *diacetyl* derivative forms small, white crystals, which decompose without previous fusion. 1:3:5-*Trihydroxy*-2:4:6-tridinaphthaxanthyl benzene,



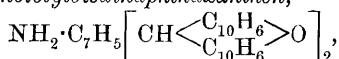
crystallises from acetic acid in beautiful, colourless needles, decomposes without fusion, is soluble in alcoholic, and insoluble in aqueous alkali hydroxides; it yields a *triacetate*, which melts at 270° and crystallises from toluene in beautiful, white crystals. 1:5-*Dihydroxy*-2-dinaphthaxanthylbenzene, $\text{OH} \cdot \text{C}_6\text{H}_3 \cdot \text{C}_{21}\text{H}_{13}\text{O}$, decomposes below 300° , is soluble in aqueous alkali hydroxides, and yields a *diacetyl* derivative which melts at $230-231^\circ$ and crystallises from toluene in white crystals. 1-*Hydroxy*-3-diethylamino-4:6-bis(dinaphthaxanthyl) benzene, $\text{OH} \cdot \text{C}_6\text{H}_2(\text{C}_{21}\text{H}_{13}\text{O})_2 \cdot \text{NEt}_2$, obtained from dinaphthaxanthonium bromide and *m*-diethylaminophenol, forms small crystals becoming

violet, melts at 250—252°, and is soluble in alcoholic but insoluble in aqueous alkali hydroxides. M. A. W.

Dinaphthapyranic [Dinaphthaxanthyl] Derivatives containing Nitrogen. A. ROBYN (*Compt. rend.*, 1905, 140, 1644. Compare Fosse, Abstr., 1904, i, 337).—*Aminophenyl*dinaphthaxanthen,



prepared by condensing aniline with dinaphthaxanthonium hydrobromide (*loc. cit.*), forms colourless crystals, melts and decomposes at 250—253°, is soluble in benzene and insoluble in alcohol. *o*-Aminotolyl-dinaphthaxanthen, similarly prepared, resembles the foregoing and melts at 270—271°; the isomeride derived from *p*-toluidine melts at 232—233°. *m*-Aminotolylbisdinaphthaxanthen,



melts at 275° and is less soluble in benzene than the foregoing. *α*-Naphthylaminodinaphthaxanthen forms slightly coloured crystals and melts at 255—260°. T. A. H.

Action of Methyl Iodide on Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, 140, 1601—1603. Compare Abstr., 1903, i, 717; 1904, i, 187; Wackernagel and Wölffenstein, 1903, i, 917; Willstätter and Marx, 1904, i, 613; Semmler, 1904, i, 685; Scholtz and Pawlicki, 1904, i, 1045).—When a mixture of sparteine, methyl iodide, and methyl alcohol after remaining for 24 hours is heated for one hour, a mixture of two methiodides is produced. *α*-Sparteine methiodide is identical with Bamberger's substance (Abstr., 1887, 163); *α'*-sparteine methiodide was not obtained free from the *α*-isomeride, but is distinguished from it in being more soluble in water and in having a higher specific rotation, $[\alpha]_D - 36.9^\circ$.

The formation of sparteine methiodide hydriodide in Scholtz and Pawlicki's experiments is due to the liberation of hydrogen iodide by the interaction of the methyl iodide and methyl alcohol used. In this case hydriodides of the two isomeric methiodides are formed. The salt of the *α*-methiodide has $[\alpha]_D - 17.1^\circ$ in water, and the best preparation of the hydriodide of the *α*-isomeride obtained had $[\alpha]_D - 46.3^\circ$. A small quantity of sparteine hydriodide $[\alpha]_D - 11.06^\circ$ in methyl alcohol) is also formed in this reaction. T. A. H.

Stereoisomerism of Sparteine Methiodides. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, 140, 1645—1647).—When either of the two isomeric sparteine methiodide hydriodides produced by Scholtz and Pawlicki's process (Abstr., 1904, i, 1045, and preceding abstract) is heated, it yields methyl iodide and sparteine hydriodide, the only difference being that the *α'*-isomeride undergoes this decomposition at a slightly lower temperature than the salt of the *α*-methiodide. Further, when sparteine hydriodide is heated with excess of methyl iodide at 136° a mixture of the two sparteine methiodide hydriodides is formed. These observations indicate that these two substances are stereoisomerides, and that in both salts the methyl

iodide is attached to the same nitrogen atom and the hydrogen iodide to the other.
T. A. H.

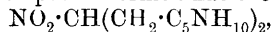
Action of Ethyl Iodide on Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, 141, 49—51. Compare Scholtz and Pawlicki, *Abstr.*, 1904, i, 1045, and preceding abstracts).—When sparteine reacts with ethyl iodide in the absence of any solvent, sparteine hydriodide is formed and ethylene liberated. When ethyl alcohol is employed as a solvent, the reaction proceeds slowly in the cold, and more rapidly on heating in a reflux apparatus or in closed tubes. In the last two cases the products are sparteine hydriodide and two isomeric sparteine ethioides partly free and partly in the form of their hydrioides. One of the sparteine ethioides crystallises in truncated tetrahedra, is slightly soluble in cold water and more soluble in warm water or methyl alcohol, and has $[\alpha]_D - 25.42'$ in methyl alcohol. The *hydriodide* of this form crystallises from a mixture of methyl alcohol and acetone and has $[\alpha]_D - 16.08'$ in water, and on treatment with alkalis yields sparteine ethioidide, not sparteine as Bamberger supposed (*Abstr.*, 1887, 163). The isomeric *ethioidide* is very soluble in cold water and has $[\alpha]_D - 38.4'$.

The sparteine ethioidide hydriodide obtained by Mills and later by Bamberger (*loc. cit.*) is probably a mixture of the salts of the two isomeric ethioidides.

Ethyl iodide does not combine with sparteine hydriodide.

T. A. H.

Condensation of Nitromethane with Derivatives of Alkylated Aminomethyl Alcohol. LOUIS HENRY (*Ber.*, 1905, 38, 2027—2031).—When nitromethane is condensed with 1-hydroxymethylpiperidine, the compound formed has the formula



and not $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_3$ as was formerly supposed by the author (*Bull. Acad. roy. Belg.*, 1896, [iii], 32, 33).

The compound $\text{NO}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{NMe}_2)_2$, formed by the condensation of nitromethane with dimethylaminomethyl alcohol, crystallises in nacreous leaflets and melts at $56-57^\circ$.

The compound $\text{OH} \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_2 \cdot \text{NO}_2$, formed by the action of formaldehyde on the compound $\text{NO}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_2$, melts at $101-102^\circ$. It may also be formed by the action of piperidine (1 mol. or 2 mols.) on the product resulting from the action of formaldehyde (3 mols.) on nitromethane (1 mol.) or by the action of 1-hydroxymethylpiperidine on nitroethyl alcohol. An *isomeride*, melting at $78-79^\circ$ and crystallising from ether in needles, is formed when the former compound is submitted to further treatment with a solution of piperidine in hot alcohol.

A. McK.

Isomeric Oxypyridines from β -Ketones. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1904—1905, 40, 493—506. Compare Guareschi, *Abstr.*, 1900, i, 52).—In presence of ammonia, the β -ketones condense with ethyl cyanoacetate, yielding cyanopyridones (Guareschi, *loc. cit.*); and where the condensed radicles are identical only one com-

pound is obtained, but where these radicles are different two isomeric compounds may be obtained, the isomerism depending on the two different positions which the carbonyl groups may assume in the condensation. The author has examined the products obtained with benzoylacetone and with acetylmethyl hexyl ketone, and by distillation with zinc dust has been able to establish their constitutions.

The condensation of benzoylacetone with ethyl cyanoacetate in presence of ammonia yields: (1) benzoylacetoneamine or benzoylacetoneimine, formed by the action of ammonia on benzoylacetone; (2)

5-cyano-6-oxy-4-phenyl-2-methyldihydropyridine, $\text{CPh} \begin{smallmatrix} \text{CH}_2\text{-CMe} \\ \diagdown \quad \diagup \\ \text{C(CN)} \cdot \text{CO} \end{smallmatrix} \text{N}$,

which crystallises from alcohol in slender, white, anhydrous needles melting at $263\text{--}264^\circ$, and dissolves slightly in water or acetone; (3)

5-cyano-6-oxy-2-phenyl-4-methyldihydropyridine, $\text{CMe} \begin{smallmatrix} \text{CH}_2\text{-CPh} \\ \diagdown \quad \diagup \\ \text{C(CN)} \cdot \text{CO} \end{smallmatrix} \text{N}$,

which crystallises from alcohol in shining, nacreous plates exhibiting a slight blue fluorescence and melting at 310° ; it is sparingly soluble in water, and, like the preceding compound, is soluble in dilute alkali hydroxide solutions, from which it is reprecipitated on acidification. They both reduce potassium permanganate energetically, hydrogen cyanide being evolved.

The condensation of acetylmethyl hexyl ketone with ethyl cyanoacetate in presence of ammonia yields: (1) *5-cyano-6-oxy-2-methyl-4-*

hexylpyridine, $\text{C}_6\text{H}_{13} \cdot \text{C} \begin{smallmatrix} \text{CH}_2\text{-CMe} \\ \diagdown \quad \diagup \\ \text{C(CN)} \cdot \text{CO} \end{smallmatrix} \text{N}$, which crystallises in large,

shining plates having a soapy feel and melting at 108° , and is soluble in alcohol, ether, acetone, or benzene; (2) *5-cyano-6-oxy-4-methyl-2-hexyl-*

pyridine, $\text{CMe} \begin{smallmatrix} \text{CH}_2\text{-C(C}_6\text{H}_{13}) \\ \diagdown \quad \diagup \\ \text{C(CN)} \text{---} \text{CO} \end{smallmatrix} \text{N}$, which crystallises from aqueous

alcohol in slender needles melting at $193\text{--}194^\circ$, dissolves in alcohol, ether, acetone, or benzene, and when powdered in a mortar readily becomes electrified.

From the above results the author concludes: (1) that a β -diketone containing two different radicles, on condensation with ethyl cyanoacetate in presence of ammonia, yields two well-defined isomerides; that the melting point and solubility of these compounds rise as the radicle with the higher molecular weight approaches the nitrogen atom; that with an equal number of carbon atoms the more highly hydrogenated oxypyridines have the lower melting points.

T. H. P.

Action of Formaldehyde on 1:2-Dimethyl- Δ^2 -tetrahydropyridine. ANDREAS LIPP and EDUARD WIDMANN (*Ber.*, 1905, 38, 2276—2283. Compare Lipp, *Abstr.*, 1892, 1244; 1897, i, 229; Lipp and Richard, *Abstr.*, 1904, i, 342; Ladenburg, *Abstr.*, 1893, i, 426; 1898, i, 687).—The base obtained by the condensation of formaldehyde with 1:2-dimethyl- Δ^2 -tetrahydropyridine, reduction of the product with sodium and alcohol, elimination of water by the action of hydrochloric acid, and reduction of the resulting vinyl derivative with tin and hydrochloric acid, is identical with 1-methyl-3-ethylpiperidine formed from Stoehr's 3 ethylpiperidine (*Abstr.*,

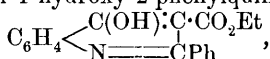
1892, 628) by treatment with methyl iodide, conversion of the methiodide into the methochloride, and distillation of this at 240—250°. The properties of the bases prepared by these two series of reactions, and of the hydrochloride obtained from them, agree with those given for 1-methyl-3-ethylpiperidine and its hydrochloride by Ladenburg (Abstr., 1898, i, 688). The following salts were prepared from the bases of both origins: the aurichloride crystallises in sheaves of long needles and melts at 100—101° (m. p. 104—105°; Ladenburg, *loc. cit.*); the platinichloride, $(C_7H_{14}NMe)_2 \cdot H_2PtCl_6$, crystallises in orange-red, glistening prisms and melts at 145—148°; the *mercurichloride*, $(C_7H_{14}NMe, HCl)_2 \cdot 3HgCl_2$, forms long, glistening needles and melts at 91—92°; the *picrate*, $C_8H_{17}N, C_6H_3O_7N_3$, crystallises in long needles and melts at 133—134°; the *methiodide*, $C_7H_{14}NMe, MeI$, crystallises in glistening octahedra or matted needles, and melts at 194—195° or at 197—198°; a mixture of the two methiodides of different genesis melted at 195—196°; the *methochloride* crystallises in stellate groups of needles and is deliquescent; the *aurichloride* of the methochloride, $C_7H_{14}NMe, MeCl, AuCl_3$, forms glistening, yellow leaflets and melts at 135—137°; the *platinichloride* of the methochloride, $(C_7H_{14}NMe, MeCl)_2 \cdot PtCl_4$, crystallises in glistening needles or prisms and melts and decomposes at 250° or at 255°. G. Y.

Indoline. GIUSEPPE PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1905, 14, i, 632—637).—*Indoline*, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} CH_2$, prepared by heating 1-methylindoline in a sealed tube with phosphorus and hydriodic acid at 210—230°, is a colourless, faintly-smelling base lighter than water and boils at 220—221°; it can be kept for a long time without change, and in dilute sulphuric acid solution gives no coloration with nitrous acid. Its *picrate*, $C_{14}H_{12}O_7N_4$, separates from alcohol in minute crystals melting at 174°; its *hydrochloride* was prepared, and its *platinichloride*, $(C_8H_9N)_2 \cdot H_2PtCl_6$, which forms a yellow precipitate afterwards turning red, and decomposes without melting at about 180°; its *acid oxalate*, $C_{10}H_{10}O_4N$, separates from alcohol in colourless crystals melting at 128°.

1-*Benzoylindoline*, $C_{15}H_{13}O_2N$, separates from ethyl acetate in colourless, refractive, prismatic crystals melting at 118—119°.

1-*Nitrosoindoline*, $C_8H_8ON_2$, crystallises from light petroleum in faintly yellow scales melting at 83—84°, and exhibits normal cryoscopic behaviour in benzene solution; it gives the nitrosoamine reactions with Liebermann's reagent and with a sulphuric acid solution of diphenylamine, and, when treated with hydroxylamine hydrochloride, yields the original indoline. T. H. P.

Synthesis of Quinoline Derivatives. III. Action of Ethyl Benzoylacetate on Anthranilic Acid. STEFAN VON NIEMEN-TOWSKI (*Ber.*, 1905, 38, 2044—2051. Compare Abstr., 1894, i, 427; 1896, i, 187).—Ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate,



is the main product obtained when anthranilic acid and ethyl benzoylacetate in molecular proportion are heated for 50 hours at 140—150°. It forms rectangular rods and melts and decomposes at 262°. The compound $C_{32}H_{20}O_5N_2$ is obtained as a by-product, which crystallises in yellow needles and melts at 308°.

When the condensation of ethyl benzoylacetate with anthranilic acid is conducted for 250 hours, the temperature finally being raised to 180°, *s*-triphenylbenzene, $C_{24}H_{18}$, crystallising in yellow needles and melting at 171°, is one of the products. Its formation is expressed by the equation $3CH_2Bz \cdot CO_2Et = C_{24}H_{18} + 3CO_2 + 2EtOH$. Ethyl 4-hydroxy-2-phenylquinoline-3-carboxylate is also formed in small yield in this case.

A. McK.

A New Class of Quinoline Dyes. II. EMIL BESTHORN and J. IBELE (*Ber.*, 1905, 38, 2127—2129. Compare Abstr., 1904, i, 527).—The red dye previously described may be prepared by the action of the chloride of quinaldinic acid on quinoline in dry benzene solution. The chloride of quinaldinic acid, obtained by the action of thionyl chloride, crystallises from light petroleum in needles, melts and turns brown at 97—98° and not at 175—177° as stated by H. Meyer (this vol., i, 155). It dissolves readily in ether or benzene and when boiled with water yields a red dye.

J. J. S.

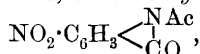
isoNitrosomethylisooxazolone. LOUIS BOUVEAULT and ANDRÉ WAHL (*Ber.*, 1905, 38, 2066—2067).—A reply to Hantzsch (this vol., i, 408).—The authors confirm Jovitschitsch's results (Abstr., 1896, i, 82), which contradict those of Nussberger (Abstr., 1892, 1175). When recrystallised from water, *isonitrosomethylisooxazolone* forms anhydrous leaflets and melts at 159°.

G. Y.

Derivative of Glycuronic Acid and *p*-Nitrophenylhydrazine. A Correction. AN. K. MEDVEDEFF (*Ber.*, 1905, 38, 2283. Compare this vol., i, 491).—The compound $C_{18}H_{22}O_5N_6$, described in the previous paper, is now found to be the *p*-nitrophenylhydrazone of acetaldehyde.

G. Y.

Synthesis of 5-Nitro-4-ketodihydroquinazolines from 6-Nitro-2-aminobenzoic Acid, 6-Nitro-2-acetylaminobenzoic Acid, and from the corresponding Nitroacetylanthranil. MARSTON T. BOGERT and VICTOR J. CHAMBERS (*J. Amer. Chem. Soc.*, 1905, 27, 649—658).—6-Nitro-2-aminobenzoic acid is best prepared by the action of potassium hypobromite on 3:1-nitrophthalamic acid as described by Kahn (Abstr., 1903, i, 94). When the acid is boiled with excess of acetic anhydride, 6-nitroacetylanthranil,



is produced which crystallises in large, colourless plates or prisms, melts at 155—156° (corr.), is soluble in acetone or hot chloroform, and reacts readily with primary amines to form substituted anthranilamides which easily condense to quinazolines.

6-Nitro-2-acetylaminobenzoic acid, $NO_2 \cdot C_6H_3(NHAc) \cdot CO_2H$, obtained by adding nitroacetylanthranil to boiling water, forms large prismatic

crystals, melts and decomposes at 212—214°, and is soluble in water, acetone, or hot alcohol, and slightly so in warm chloroform or benzene.

5-Nitro-4-ketodihydroquinazoline, $\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{NH} \end{array}$, obtained by heating ammonium 6-nitro-2-aminobenzoate with formamide at 150—160°, crystallises in colourless needles, melts and decomposes at 255—256° (corr.), and is soluble in hot water, alcohol, or acetone. The colourless needles which separate from a hot aqueous solution gradually change into pale green prisms of the same melting point and solubility, the change being complete in 24—36 hours. The *hydrochloride*, *platinichloride*, and *nitrate* are described.

5-Nitro-4-keto-2-methyldihydroquinazoline, $\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{CMe} \\ | \quad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{NH} \end{array}$, may be prepared by heating 6-nitro-2-aminobenzoic acid with acetic anhydride and acetonitrile in a sealed tube for 6 hours at 160—170°. It can also be obtained by the action of heat on ammonium 6-nitro-2-acetylaminobenzoate, or by dissolving nitroacetylanthranil in dilute ammonia and acidifying the solution with acetic acid. The compound crystallises from alcohol in slender, colourless needles, melts and decomposes at 277—279° (corr.), and is soluble in warm acetone or alcohol and slightly so in hot water; the *chloride* and *nitrate* are described.

5-Nitro-4-keto-3-phenyl-2-methyldihydroquinazoline, $\begin{array}{c} \text{CH} \cdot \text{CH} = \text{C} \cdot \text{N} = \text{CMe} \\ | \quad | \\ \text{CH} \cdot \text{C}(\text{NO}_2) : \text{C} \cdot \text{CO} \cdot \text{NPh} \end{array}$, obtained by heating nitroacetylanthranil with excess of aniline and boiling the product with water acidified with acetic acid, crystallises from alcohol in cubes, melts at 233—234° (corr.), and is easily soluble in warm acetone or hot nitrobenzene. E. G.

New Series of Dihydroquinoxalines. JOHN B. EKELEY and ROBERT J. WELLS (*Ber.*, 1905, **38**, 2259—2264).—2-Methyl-3-isopropyl-1:4-dihydroquinoxaline, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad | \\ \text{NH} \cdot \text{CPr} \end{array}$, is formed by the

action of hydrogen chloride on a mixture of *o*-phenylenediamine and acetone or mesityl oxide, or by heating *o*-phenylenediamine and mesityl oxide with phosphorus pentachloride at 160°, or when the diamine and mesityl oxide are heated together in molecular amounts in benzene; the free base is obtained from its hydrochloride by treatment with aqueous alkali hydroxides. It crystallises in large, monoclinic prisms or large, thin leaflets, melts at 124°, and dissolves in alcohol, ether, chloroform, carbon disulphide, hydrocarbons, or acids to colourless solutions which become yellow on warming. The *hydrochloride*, $\text{C}_{12}\text{H}_{16}\text{N}_2 \cdot 2\text{HCl}$, and the *hydrobromide*, $\text{C}_{12}\text{H}_{16}\text{N}_2 \cdot 2\text{HBr}$, are obtained in long, colourless needles on evaporation of their aqueous solutions, but on addition of the hydrogen haloids to benzene solutions of the base, lemon-yellow crystalline powders are obtained, the hydrobromide having the constitution $\text{C}_{12}\text{H}_{16}\text{N}_2 \cdot \text{HBr}$. The *sulphate* is very soluble in water, and on evaporation of its solution decomposes into mesityl oxide and *o*-phenylenediamine sulphate. The *picrate*, $\text{C}_{12}\text{H}_{16}\text{N}_2 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms yellow crystals; the *platinichloride*, $(\text{C}_{12}\text{H}_{16}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, is

yellow. With sodium nitrite in glacial acetic acid solution, the base forms a *dinitroso*-derivative, $C_{19}H_{14}N_2(NO)_2$, which crystallises from ether in yellow needles, melts at 177° , and gives Liebermann's nitroso-reaction. The *dibenzoyl* derivative crystallises in small, yellow needles, softens at $85-90^\circ$, and decomposes at about 175° . The base is not reduced by sodium and boiling alcohol; with oxidising agents it yields a quin-oxaline and sometimes a green fluorescent dihydroquinoxaline. With mercuric chloride the base forms a yellow, with copper sulphate a light green, precipitate.

o-Xylylenediamine, but not *o*-tolylenediamine, reacts with mesityl oxide to form a 1 : 4-dihydroquinoxaline. G. Y.

Laws of Substitution in Aromatic Compounds. BERNHARD FLÜRSCHHEIM (*J. pr. Chem.*, 1905, [ii], 71, 497—539. Compare Abstr., 1903, i, 79; Holleman, Abstr., 1903, i, 623; Kauffmann, Abstr., 1903, ii, 401).—The author replies to the criticisms of Holleman and of Kauffmann, and extends the application of the ideas underlying his law of substitution, to the formation of 1 : 4-additive compounds by substances containing conjugated ethylene linkings, to the constitution of triphenylmethyl, and to the formation of stereoisomerides.

The formation of azoxy-compounds by the reduction of nitro-compounds is preceded by the formation of an additive compound by the hydroxylamine and nitroso-compound which are the primary reduction products. The formation of the additive compound cannot take place if the nitrogen atom of the hydroxylamine is already pentavalent owing to salt formation, which, and not the velocity of the reduction (compare Goldschmidt and Ingebrechtsen, Abstr., 1904, ii, 608), is the cause of the non-appearance of azoxy-, azo-, or aminoazo-benzene in the reduction of nitrobenzene in acid solution. If negative groups are introduced into the benzene nucleus, as in *m*-dinitrobenzene, *s*-trinitrobenzene, or di-*m*-chloro-*p*-bromonitrobenzene, the hydroxylamine salt formed on reduction in acid solution is more or less dissociated, the additive compound is formed to a corresponding extent, and the reduction product is a mixture of the azoxy-, azo-, aminoazo-, and amino-compounds. The reduction of ethyl *m*-nitrobenzenesulphonate with stannous chloride and hydrochloric acid leads to the formation of the amine only, whilst under the same conditions *m*-nitrobenzenesulphonic chloride yields *m*-nitrobenzenesulphinic acid.

Di-*m*-chloro-*p*-bromonitrobenzene, $C_6H_2Cl_2Br \cdot NO_2$, is formed by the action of hydrogen bromide and sodium nitrite on 2 : 6-dichloro-4-nitroaniline in warm glacial acetic acid solution; it is colourless, melts at $87-88^\circ$, and is only slightly volatile in a current of steam.

3 : 3' : 5 : 5'-Tetrachloro-4 : 4'-dibromoazoxybenzene, $C_{12}H_4ON_2Cl_4Br_2$, crystallises in characteristic groups of yellow needles and melts at $220-221^\circ$.

3 : 5-Dichloro-4-bromoaniline, $C_6H_4NCl_2Br$, crystallises in colourless needles, melts at 126° , and forms a sparingly soluble *sulphate*.

The reduction of 3 : 3'-dinitroazoxybenzene with stannous chloride and hydrochloric acid in alcoholic solution leads to the formation of 3 : 3'-diaminoazoxybenzene but not of *m*-nitroaniline. The primary

products in the reduction of nitro-compounds by ammonium sulphide cannot be hydroxylamines and nitroso-compounds, as whilst *m*-nitroaniline is formed from *m*-dinitrobenzene, no trace of it is obtained on treating with ammonium sulphide 3 : 3'-dinitroazoxybenzene, which is formed by reduction of *m*-dinitrobenzene with sodium sulphide.

Acetyl-s-dinitroanilide, $C_8H_7O_5N_3$, crystallises in needles and melts at 186—187°. *s-Nitrophenylenediamine*, $C_6H_7O_2N_3$, is formed by reduction of *s*-trinitrobenzene or of *s*-dinitroaniline with ammonium sulphide in boiling alcoholic solution; it is purple-red, melts at 140—141°, and forms a *diacetyl* derivative, $C_{10}H_{11}O_4N_3$, melting at 270°. G. Y.

Isomerism of the so-called Ethyl Benzeneazocyanoacetate.

ARTHUR HANTZSCH and K. J. THOMPSON (*Ber.*, 1905, 38, 2266—2276. Compare Weissbach, *Abstr.*, 1903, i, 541).—Weissbach's supposed stereoisomeric ethyl benzeneazocyanoacetates were the α - and β -modifications of ethyl phenylhydrazonocyanoacetate containing traces of formazyl cyanide, which is formed from diazonium salts and ethyl cyanoacetate in strongly alkaline solution.

When free from the α -modification, ethyl β -phenylhydrazonocyanoacetate melts at 85—86°.

That the two modifications of ethyl phenylhydrazonocyanoacetate are stereoisomeric is shown by the occurrence of one modification only of the following symmetrical hydrazones:

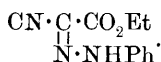
Ethyl phenylhydrazonemesoxalate, $NHPh \cdot N : C(CO_2Et)_2$, formed by the action of diazonium salts on ethyl malonate in presence of sodium acetate in aqueous-alcoholic solution, is an oil; it is hydrolysed by 1 mol. of alkali hydroxide at the laboratory temperature to ethyl hydrogen phenylhydrazonemesoxalate, melting at 114°.

Ethyl p-bromophenylhydrazonemesoxalate crystallises in yellow needles and melts at 76°.

Methyl phenylhydrazonemesoxalate (von Pechmann, *Abstr.*, 1895, i, 329) is easily hydrolysed by aqueous alkali hydroxides; hydrolysis with 1 mol. of alkali hydroxide in ethyl alcoholic solution leads to the formation of a mixture of the monomethyl and monoethyl esters.

The phenylhydrazone of mesoxalonitrile crystallises with $\frac{1}{2}$ mol. of benzene and decomposes at 146—147° (compare Schmidtman, *Abstr.*, 1896, i, 458).

In its acidity and in its behaviour towards acetylisng agents, ethyl α -phenylhydrazonocyanoacetate resembles the phenylhydrazone of mesoxalonitrile, whilst the β -modification resembles the esters of phenylhydrazonemesoxalic acid: to the α -modification, therefore, is to be ascribed the configuration
$$\begin{array}{c} CN \cdot C \cdot CO_2Et \\ | \\ NHPh \cdot N \end{array}$$
, and to the β -modification

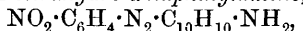


The protection of the carboxylic group by the proximity of the group $-NHPh$ explains the formation of phenylhydrazonemesoxalic acid in hydrolysis of the β -form with sodium carbonate, whilst under the same conditions the α -form yields phenylhydrazonегlyoxylic acid. G. Y.

Azo-colouring Matters derived from *ar*-Tetrahydro-*a*-Naphthylamine. GILBERT T. MORGAN and F. E. RICHARDS (*J. Soc. Chem. Ind.*, 1905, **24**, 652. Compare *Trans.*, 1904, **85**, 736).—I. Azo- and Disazo-derivatives of *ar*-Tetrahydro-*a*-naphthylamine.—*ar*-Tetrahydro-*a*-naphthylamineazobenzenesulphonic acid dyes wool an orange shade from an acid-bath; its sodium salt crystallises in brownish-orange scales; after diazotising, it condenses with 1:8-dihydroxynaphthalene-3:6-disulphonic acid to yield a disazo-compound of the formula $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_{10}\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_3(\text{OH})_2(\text{SO}_3\text{Na})_2$, which when dyed on wool from an acid-bath gives reddish-violet shades; it condenses in the same way with "*R*-salt," and with *a*-naphthol-4-sulphonic acid, forming disazo dyes which give reddish-brown shades.

Naphthaleneazo-ar-tetrahydro-a-naphthylamine, $\text{C}_{10}\text{H}_7\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_{10}\cdot\text{NH}_2$, obtained by condensing diazotised *a*-naphthylamine with *ar*-tetrahydro-*a*-naphthylamine, separates from methyl alcohol in reddish-black nodular crystals.

p-Nitrobenzeneazo-*ar*-tetrahydro-*a*-naphthylamine,



is produced by adding an acetic acid solution of *p*-nitrobenzene-diazonium chloride to an alcoholic solution of *ar*-tetrahydro-*a*-naphthylamine, and liberating the base from the hydrochloride so formed by ammonia; it crystallises from ethyl acetate in dark brown flakes.

Tetrahydro-a-naphthaleneazo-ar-tetrahydro-a-naphthylamine, obtained by condensing diazotised tetrahydro-*a*-naphthylamine with another molecular proportion of the base in acetic acid solution, crystallises from ethyl acetate in brownish-orange needles melting at 135—140°.

II. Substantive Polyazo-colouring Matters from *ar*-Tetrahydro-*a*-naphthylamine.

Ditolyldisazo-ar-tetrahydro-a-naphthylamine, $\text{C}_{14}\text{H}_{12}(\text{N}_2\cdot\text{C}_{10}\text{H}_{10}\cdot\text{NH}_2)_2$, is formed from *ar*-tetrahydro-*a*-naphthylamine (2 mols.) and tetrazotised tolidine. It dissolves in alcohol to an orange-brown solution; its hydrochloride is a black powder which dissolves in alcohol to a purple solution. This hydrochloride on diazotising combines with 1:8-dihydroxynaphthalene-3:6-disulphonic acid and with *a*-naphthol-4-sulphonic acid to form black powders with metallic lustre which are sparingly soluble in cold water to a reddish-violet solution, and develop intense blue colorations with concentrated sulphuric acid. The former gives greyish-blue shades on unmordanted cotton, and the latter heliotrope tints.

The diazo-compound, obtained by condensing one molecule of the tetrahydro-base with tetrazotised tolidine, when again diazotised and coupled with 1:8-dihydroxynaphthalene-3:6-disulphonic acid or with *a*-naphthol-4-sulphonic acid, gives rise to dyes which colour unmordanted cotton dark blue and reddish-heliotrope respectively.

III. Azo-derivatives of *ar*-Tetrahydro-*a*-naphthylamine-4-sulphonic Acid.

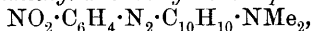
Most of the points dealt with under this head have been already published in *Trans.*, 1904, **85**, 736.

IV. Azo-derivatives of Dimethyl-*ar*-tetrahydro-*a*-naphthylamine.

Dimethyl-ar-tetrahydro-a-naphthylamine was prepared by heating

ar-tetrahydro- α -naphthylamine hydrochloride with methyl alcohol at 170—180°.

p-Nitrobenzeneazodimethyl-*ar*-tetrahydro- α -naphthylamine,



produced by coupling the base with *p*-nitrobenzenediazonium chloride, crystallises from alcohol in well-defined, deep red acicular prisms melting at 150—152°.

*Sodium dimethyl-*ar*-tetrahydro- α -naphthylamineazobenzenesulphonate*, $\text{NMe}_2 \cdot \text{C}_{10}\text{H}_{10} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$, prepared by coupling the base with diazobenzenesulphonic acid, separates from aqueous solution in yellow-brown flakes. It gives red shades on wool from an acid-bath.

Throughout the paper the colours produced by the various dyes are compared with those obtained from the corresponding naphthalene analogues, and as a result the following conclusions are arrived at:

(1) *ar*-Tetrahydro- α -naphthylamine resembles α -naphthylamine in yielding directly aminoazo-compounds from which polyazo-colouring matters may be obtained.

(2) The azo- and disazo-colouring matters derived from *ar*-tetrahydro- α -naphthylamine, its sulphonic acid and dimethyl derivative, resemble their analogues of the benzene series in tinctorial properties, but differ from those of the naphthalene series.

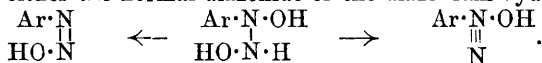
P. H.

Normal Diazoxides as Primary Products of the Interaction of Nitrosobenzenes and Hydroxylamine. ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 2056—2062. Compare *Abstr.*, 1903, i, 664; 1904, i, 201; Bamberger, *Abstr.*, 1895, i, 459; 1900, i, 531).—A mixture of nitrosobenzene and α -naphthol in alcoholic solution was treated with a concentrated aqueous solution of hydroxylamine hydrochloride, then with a concentrated sodium carbonate solution, and diluted finally with water; immediate “coupling” took place, and the α -naphthol-dye was obtained in a yield of 56 per cent. of the theoretical. In a similar experiment with β -naphthol, a 53 per cent. yield of the dye was obtained. In a third, an aqueous solution of 1 mol. of hydroxylamine hydrochloride and 1 mol. of potassium hydroxide was added slowly to an alcoholic solution of 1 mol. of nitrosobenzene and excess of β -naphthol; a 48 per cent. yield of the dye was obtained, and no *anti*-diazoxide could be detected in the filtrate.

Contrary to Bamberger’s statement, therefore, the primary product of the interaction of nitrosobenzene and hydroxylamine is the normal diazoxide. The failure to obtain more than traces of the dye under Bamberger’s conditions is due to the instability of nitrosobenzene, as also of the normal diazoxides in alkali hydroxide solutions. Even on addition of a neutral solution of hydroxylamine hydrochloride and sodium hydroxide to a solution of nitrosobenzene at -10° , evolution of nitrogen ensues, and only traces of the dye are formed on subsequent addition of β -naphthol.

Similar results are obtained with bromonitrosobenzene: in neutral solution at -10° , and with subsequent addition of β -naphthol, only traces of the dye; but in neutral solution, in presence of β -naphthol, 31 per cent., and in presence of β -naphthol and excess of sodium carbonate, 48 per cent., of the dye is obtained. At -5 — 0° , with

excess of potassium hydroxide, no trace of the dye, but *p*-dibromo-azoxybenzene is obtained. These results are brought into agreement with the views of Angeli (Abstr., 1904, i, 699) if the action of hydroxylamine on nitrosobenzene is represented as resulting in the formation of the additive compound, which on elimination of water may yield either the normal diazoxide or the diazonium hydroxide:



G. Y.

Velocity of Decomposition of *p*-Nitrobenzenediazonium-chloride. CARL SCHWALBE (*Ber.*, 1905, 38, 2196—2199).—Cain and Nicoll's formula (*Trans.*, 1902, 81, 1412) for the decomposition of aromatic diazo-compounds does not hold when applied to technical products in which free nitrous acid and salts are generally present. Nitrous acid very materially hastens the rate of decomposition of diazo-compounds; salts, on the other hand, increase their stability. They are also much less stable in concentrated solution than in dilute.

E. F. A.

Action of Diazo-compounds on Primary Aliphatic Amines. OITO DIMROTH (*Ber.*, 1905, 38, 2328—2330).—Whilst molecular amounts of diazo-compounds and primary aromatic amines unite to form diazoamino-compounds, and bisdiazo-compounds are formed only rarely, it was found by Goldschmidt and Badl (Abstr., 1889, 774) that bisdiazo-compounds only were formed by the action of aromatic diazonium salts on methylamine, ethylamine, and allylamine.

Since the author has shown (this vol., i, 311) that fatty aromatic triazens are very labile, it appeared possible that the formation of these compounds had not been observed during the action of diazo-compounds on primary aliphatic amines owing to their instability.

It is now shown that the first phase of the action of a diazonium salt on a primary aliphatic amine consists in the formation of a triazen, which is readily distinguished from a bisdiazoamino-compound by the action of acids on it, when nitrogen is evolved in the cold.

The preparation of phenylmethyltriazen (compare Abstr., 1903, i, 450; and this vol., i, 311) from benzenediazonium chloride and methylamine is described, as also is the preparation of phenylethyltriazen (compare this vol., i, 311) from benzenediazonium chloride and ethylamine.

A. McK.

Colour Reactions of Proteids with *p*-Dimethylaminobenzaldehyde and other Aromatic Aldehydes. ERWIN ROHDE (*Zeit. physiol. Chem.*, 1905, 44, 161—170).—A pale-red coloration is obtained when a 2 per cent. solution of *p*-dimethylaminobenzaldehyde in normal hydrochloric acid is added to ordinary urine, and with certain pathological urines a deep-red coloration is produced. Proteids also yield similar colorations with the aldehyde in presence of concentrated acids. It is now shown that this coloration is due to the indole group

present in the proteids, and gluten which contains no indole nucleus gives no coloration. Hopkins and Cole's tryptophan, scatoleaminoacetic acid (Abstr., 1902, i, 193) or indoleaminopropionic acid (Ellinger, Abstr., 1904, i, 640), gives the same coloration with great readiness in the presence of concentrated hydrochloric acid, but not always in the presence of concentrated sulphuric acid.

Glycine, alanine, aspartic acid, serine, lysine, arginine, histidine, cystine, glucosamine, and aminovaleric acid do not give the coloration. The following proteids give the reaction: casein, edestin, protalbumose, ovalbumin, serum-albumin, and heteroalbumose. This latter also gives Adamkiewicz's reaction with glyoxylic acid, although Pick states the contrary. No coloration is given by glutine, protamine, iodoalbumin, or aldehydoalbumins, and these substances do not give the Adamkiewicz reaction.

The red coloration is formed at the expense of the aldehydo-group, and colorations are given by all aromatic aldehydes which have been examined, but not by open-chain aldehydes or furfuraldehyde.

J. J. S.

Diamino-acids in Casein and Gelatin. A Correction. ZDENKO H. SKRAUP (*Monatsh.*, 1905, 26, 683. Compare Abstr., 1904, i, 538, 594; this vol., i, 398).—It is now found that the products of the hydrolysis of casein and gelatin previously described as diamino adipic and diamino glutaric acids are *d*-alanine and a mixture of *d*-alanine and glycine respectively.

Commercial casein, purified by Hammarsten's method, gives the alanine glycine mixture, whilst caseins of other origin yield pure alanine. G. Y.

Oxidation of Gelatin and of Egg-albumin with Calcium Permanganate. JOHN SEEMANN (*Zeit. physiol. Chem.*, 1905, 44, 229—264. Compare Kutscher and Zickgraf, Abstr., 1903, i, 666; Kutscher and Schenck, Abstr., 1904, i, 955; this vol., i, 251; Otori, this vol., i, 104; von Furth, *ibid.*, 497).—The following substances have been detected among the products obtained by the oxidation of gelatin and of egg-albumin with hot 10 per cent. calcium permanganate solution, namely: formic, acetic, butyric, and probably propionic and valeric acids; benzoic acid and benzaldehyde; oxalic and succinic acids, but not glutaric acid; oxaluramide and probably oxaluric acid. The succinic acid is probably derived from an arginine group or from those groups which yield aspartic acid when the albumins are hydrolysed. The formation of oxaluramide is accounted for by the assumption of a condensation product of an amino fatty acid and arginine, $R\cdot CH(NH_2)\cdot CO\cdot NH\cdot C(NH_2)\cdot NH\cdot [CH_2]_3\cdot CH(NH_2)\cdot CO_2H$, which, when oxidised, is ruptured at the points indicated and yields $NH_2\cdot CO\cdot CO\cdot NH\cdot CO\cdot NH_2$.

J. J. S.

Monoamino-acids of Edestin from Cotton Seeds and their Behaviour with Gastric Juice. EMIL ABDERHALDEN and OTTO ROSROSKI (*Zeit. physiol. Chem.*, 1905, 44, 265—275. Compare Abstr., 1904, i, 211).—By hydrolytic agents and by the prolonged action of

gastric juice obtained by Pawloff's method on edestin, glycine, alanine, aminovaleric acid, leucine, pyrrolidine-2-carboxylic acid, phenylalanine, aspartic acid, glutamic acid, serine, tyrosine (in small quantities), and tryptophan were obtained.

W. D. H.

Monoamino-acids from the Edestin of Sunflower Seeds.

EMIL ABDERHALDEN and BÉLA REINBOLD (*Zeit. physiol. Chem.*, 1905, **44**, 284—293).—From its decomposition products this edestin resembles others. Its behaviour to pancreatic digestion is also described.

W. D. H.

Composition of Gliadin from Wheat.

EMIL ABDERHALDEN and FRANZ SAMUELY (*Zeit. physiol. Chem.*, 1905, **44**, 276—283).—By hydrolysis with acid, gliadin yielded glycine, alanine, aminovaleric acid, pyrrolidine-2-carboxylic acid, leucine, glutamic acid, aspartic acid, phenylalanine, serine, tyrosine, tryptophan, histidine, and arginine. Lysine was absent. Of these, glutamic acid is the most abundant (27 per cent.); the other substances enumerated make up about 22 per cent.

W. D. H.

Further Researches on Protamines.

ALBRECHT KOSSEL and HENRY D. DAKIN (*Zeit. physiol. Chem.*, 1905, **44**, 342—346).—The simplest proteids, the protamines, do not yield leucine, phenylamino-propionic acid, hydroxypyrrolidinecarboxylic acid, or cystine. Sturine, however, yields leucine, but aminovaleric acid and pyrrolidine-2-carboxylic acid were not found, although these are obtained from other protamines. Scombrine appears to be the simplest proteid of all, being a combination of arginine with pyrrolidine-2-carboxylic acid and alanine.

W. D. H.

Nucleo-proteid of the Liver. IV.

JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1905, **44**, 530—539. Compare Abstr., 1903, ii, 440; 1905, i, 103).—The decomposition products of liver-nucleo-proteid found were *l*-xylose, xanthine, hypoxanthine, guanine, adenine, histidine (?), arginine, lysine, tyrosine, leucine, glycine, alanine, pyrrolidine-2-carboxylic acid, glutamic acid, aspartic acid, phenylalanine, aminohydroxysuberic acid, and diamino-hydroxysebacic acid.

W. D. H.

Preparation of Nucleic Acid.

HENRY B. SLADE (*Amer. J. Physiol.*, 1905, **13**, 464—465).—One hundred pounds of yeast are vigorously stirred with 1.1 per cent. of its weight of sodium hydroxide, dissolved in a little water and 2 or 3 times as much crystallised sodium acetate added. The mixture, after remaining at room-temperature for 24 hours, is boiled gently for an hour, and glacial acetic acid added until it is faintly acid. When cold, it is filtered and magnesium sulphate added to the filtrate to 5 per cent. strength, and then hydrochloric acid with constant stirring until a flocculent precipitate of nucleic acid forms. The presence of 2.5 per cent. of the acid usually effects a complete separation. The yield of nucleic acid is 0.5 per cent. of the yeast used; this contains 7 per cent. of phosphorus. If the method is

varied by boiling at once, the yield is less, and a nuclein compound which forms an insoluble copper compound is obtained. Under varying conditions, a series of cleavage products is formed, as Neumann found with thymo-nucleic acid. The simplest member of this series appears to be a thyminic acid. W. D. H.

[Oxidation of Nucleic Acids.] FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1905, **44**, 317—319. Compare Abstr., 1904, i, 127, and Burian, *ibid.*, 358, 956).—A discussion of the relationships between nucleic acids, nuclein bases, and uric acid. J. J. S.

Oxidation of Thymonucleic Acid with Calcium Permanganate. FRIEDRICH KUTSCHER and MARTIN SCHENCK (*Zeit. physiol. Chem.*, 1905, **44**, 309—316. Compare Kutscher and Seemann, Abstr., 1904, i, 127).—The following products have been obtained by oxidising thymonucleic acid in the form of its soluble acid barium salt with 10 per cent. calcium permanganate solution at a temperature of nearly 100°:—Oxalic, tartaric, and acetic acids, adenine, guanidine, and carbamide. *Tartaric acid*, $C_5H_8O_5N_6$ or $C_5H_{10}O_5N_6$, may be separated from the oxalic acid by means of its calcium salt; this is moderately soluble in water, from which it crystallises in fine needles. The acid crystallises in slender, microscopic needles, and does not give either the murexide or Weidel reaction. It is sparingly soluble in cold water or ether, and when heated in a melting-point tube sublimes without melting or decomposing.

Small amounts of another acid and of a biuret derivative were also isolated. J. J. S.

Protagon. N. ALBERTO BARBIERI (*Compt. rend.*, 1905, **140**, 1551—1553).—Another contribution to the much-debated question whether protagon is a chemical individual. The view taken is that protagon is non-existent in the cerebral tissues, but is a mixture of cerebrin and the substance first described by Fremy as cerebrie acid.

W. D. H.

Cerebron. HANS THIERFELDER (*Zeit. physiol. Chem.*, 1905, **44**, 366—370).—The formula given to cerebrin is $C_{48}H_{93}O_9N$. On hydrolysis, it is resolved, as shown in the following equation, into cerebronic acid, sphingosin, and galactose: $C_{48}H_{93}O_9N + 2H_2O = C_{25}H_{50}O_3 + C_{17}H_{35}O_2N + C_6H_{12}O_6$.

W. D. H.

Spectroscopy of Blood and of Oxyhæmoglobin. II. A. VILA and M. PIETRE (*Bull. Soc. chim.*, 1905, [iii], **33**, 573—580. Compare this vol., ii, 500; Bohr, Abstr., 1890, 450).—The authors have investigated the influence of various substances on the absorption spectra of solutions of blood and of oxyhæmoglobin in water. Dilute sodium chloride solution suppresses the band λ 634 in the red, a concentrated solution produces a new band, λ 597, sodium fluoride displaces the band λ 634 to a position λ 612, even in presence of other salts (compare

Menzies, Abstr., 1895, i, 256, and Ville and Derrien, this vol., i, 500), except in the case of sodium nitrite, when the displacement is to the position λ 620. The band in the red is intensified by the addition of oxidising or reducing agents; this effect is similar to that induced by drying or aging of blood or oxyhæmoglobin. The authors conclude that the colouring matter present in living blood corpuscles shows two absorption bands in the green and that it undergoes change the moment it escapes from the corpuscle and then shows the additional band λ 634 in the red, which also characterises oxyhæmoglobin. This absorption band in the red must be associated with a very stable nucleus, since it is also shown by solutions of the brown oil produced by fusing oxyhæmoglobin with potassium hydroxide.

These observations also show that oxyhæmoglobin and methæmoglobin are identical, as has already been indicated by Otto and Hüper's analyses of the two substances. T. A. H.

Methæmoglobin. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, 140, 1350—1352. Compare this vol., i, 500; ii, 402).—Polemical against Ville and Derrien, who attribute the new band described by the authors to admixture with methæmoglobin. W. D. H.

Methæmoglobin and its Fluorine Compound. JULES VILLE and EUGÈNE DERRIEN (*Compt. rend.*, 1905, 140, 1549—1551. Compare this vol., i, 500; ii, 402, and preceding abstract).—Polemical against Piettre and Vila. The view that the new absorption band is due to methæmoglobin is emphasised. The statement made by Piettre and Vila that their material cannot be methæmoglobin because it is crystallisable is shown to be incorrect. Numerous observers in the past have obtained methæmoglobin in crystalline form. W. D. H.

Carboxyhæmochromogen. FRITZ PREGL (*Zeit. physiol. Chem.*, 1905, 44, 173—181).—The statement originally made by Hoppe-Seyler, that the proportion of carbon monoxide in carboxyhæmochromogen is 1 mol. of the gas per atom of iron, is confirmed. It is also found that 5 atoms of nitrogen are present per atom of iron. Much of the present paper is devoted to the method of preparation of the hæmochromogen and the prevention of its conversion into hæmatin by the air. W. D. H.

Hæmatin. WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1905, 44, 391—421. Compare Abstr., 1896, i, 516; 1900, i, 68, 319; 1901, i, 58, 298; 1902, i, 845).—The product, insoluble in water, which is obtained by oxidising hæmatin with chromium trioxide in acetic acid solution (Abstr., 1900, i, 69) has been further investigated. The best yield (40 per cent.) is obtained when 12 atoms of oxygen are used for each molecule of hæmatin. When treated with 25 per cent. sulphuric acid or with concentrated hydrochloric acid, chromic salts and hæmatic and oxalic acids are removed and the amount of iron is considerably reduced. Some of the properties of this purified product have been examined. On further oxidation with chromium trioxide, it yields

tribasic hæmatic acid, and with nitric acid it yields oxalic, succinic, and tribasic hæmatic acid.

In the oxidation of hæmin with nitric acid, the yield of oxalic acid is greater the more concentrated the acid. The other products isolated were succinic and hæmatic acids.

Hæmatin has been oxidised with hydrogen peroxide, with sodium hypobromite, with calcium permanganate in alkaline solution, and with chromic acid in acetic acid solution, but no new products have been isolated.

Hæmatoporphyrin, when oxidised with chromic acid in sulphuric acid solution, yields the same acids, namely, oxalic, succinic, and hæmatic. In the purification of hæmatic acid as its calcium salt, a new acid has been isolated. It crystallises from hot water, contains nitrogen, does not melt at 240° , yields a readily soluble calcium salt, and gives the pyrrole reaction.

J. J. S.

Absorption of Ferments by Colloids. FERDINAND DAUWE (*Beitr. chem. Physiol. Path.*, 1905, 6, 426—453).—A discussion with some experiments on the question whether absorption or adsorption will best explain the diminution in the amount of ferment which occurs when colloids are present. Whether the union is purely physical, or whether a loose chemical compound is formed, is a question to which no clear answer is given, although it appears improbable that such different materials as coagulated proteid, animal charcoal, kieselguhr, &c., which act in the same way, form definite compounds either with ferments or colouring matters.

W. D. H.

Catalase. ALEXIS BACH (*Ber.*, 1905, 38, 1878—1885. Compare *Abstr.*, 1903, i, 671; 1904, i, 792).—The amount of hydrogen peroxide decomposed by animal catalase is found to depend both on the concentration of the peroxide and on that of the ferment. When the catalase present has reached a maximum, the amount changed is directly proportional to the quantity of hydrogen peroxide present, whilst when the hydrogen peroxide has reached a maximum, the change is directly proportional to the concentration of the ferment. The time taken by varying amounts of catalase to hydrolyse a given quantity of hydrogen peroxide decreases very much more rapidly than the quantity of ferment increases.

An attempt to compare by means of pyrogallol the distribution of hydrogen peroxide between peroxydase and catalase when both ferments are present failed, since, although the presence of catalase had no effect on the oxidation of pyrogallol by the peroxydase-hydrogen peroxide system, the pyrogallol acted injuriously on the catalase and prevented any liberation of oxygen. It is, however, also possible that, if the velocity of formation of the peroxydase-hydrogen peroxide complex is large, the peroxide will be completely withdrawn from the influence of the catalase.

E. F. A.

Mode of Action of Philocatalase. F. BATTELLI and Mlle. L. STERN (*Compt. rend.*, 1905, 140, 1352—1353. Compare this vol.,

ii, 406).—Philocatalase protects catalase in a two-fold manner, namely, by a destruction of anticatalase and a regeneration of catalase.

W. D. H.

Saccharification of Artificial Starches by Malt. EUGÈNE ROUX (*Compt. rend.*, 1905, 140, 1259—1261).—The action of malt diastase on various artificial starches (this vol., i, 262, 328) is found to be very similar to the action on flour starch. Maltose and dextrins are formed, the relative proportions of which depend on the temperature at which the action takes place. Under the same conditions, about 20 per cent. more maltose is produced from the artificial starches as compared with flour starch. The dextrins are almost completely soluble in alcohol.

H. M. D.

Influence of Liquefaction of Starch on its Transformation by Saccharifying Diastases. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1905, 140, 1067—1069).—The effect of the liquefying action of malt extract is similar to that of heat under pressure. In both cases, a considerable amount of starch remains untransformed after treatment with barley extract.

N. H. J. M.

Organic Chemistry.

Trimethylene-trisulphone and -disulphonesulphide. WALTER PETERS (*Ber.*, 1905, **38**, 2565—2567. Compare Camps, *Abstr.*, 1892, 591, 592).—The dibromide and hexabromide of trimethylenetrisulphone are represented respectively by the formulæ $\text{SBr}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{SO}_2 \\ \text{CH}_2 \cdot \text{SO}_2 \end{smallmatrix} \text{CH}_2$ and

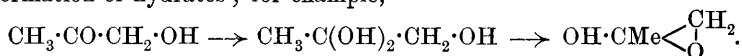
$\text{SBr}_2 \begin{smallmatrix} \text{CBr}_2 \cdot \text{SO}_2 \\ \text{CH}_2 \cdot \text{SO}_2 \end{smallmatrix} \text{CBr}_2$, as in both compounds two bromine atoms are very loosely combined. For example, the bromine atoms are removed by ammonia, by silver nitrate solution, or by sodium hydroxide in the form of hypobromite, and the compounds readily liberate iodine from a hot solution of potassium iodide.

The sodium salt of the trimethylenetrisulphone is hydrolysed to a considerable extent in aqueous solution, as shown by alkalimetric methods. J. J. S.

Aqueous Solutions of Acetylcarbinol. ANDRÉ KLING (*Bull. Soc. chim.*, 1905, [iii], **33**, 755—760).—It has already been shown (*Abstr.*, 1903, i, 138, 223) that in aqueous solution acetylcarbinol

reacts to a certain extent as the tautomeric oxide, $\text{OH} \cdot \text{CMe} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$. In the anhydrous state, however, it reacts as a ketone. Thus (a) its reaction with Grignard's reagents is perfectly normal (*Abstr.*, 1904, i, 2, 133). (b) Its molecular magnetic rotation is 3·650, and that calculated for the ketonic formula is 3·659 (Perkin, *Proc.*, 1891, 790). (c) Its molecular refraction is 17·643, corresponding with 17·614 for the ketonic formula, whereas the oxide formula requires 17·016.

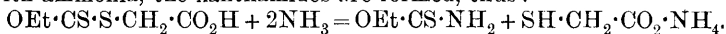
The tautomerising action of the water is attributed to the intermediate formation of hydrates; for example,



An examination of the viscosities of aqueous solutions of acetylcarbinol by Varenne and Godefroy's method (*Abstr.*, 1904, i, 2; ii, 160) indicates the formation of hydrates with H_2O , $2\text{H}_2\text{O}$, $4\text{H}_2\text{O}$, and $11\text{H}_2\text{O}$. Aqueous solutions of acetylcarbinol have a faintly acid reaction, and are only slowly neutralised by alkalis; thus the first few drops of alkali render the solution neutral, but after some time the solution again becomes feebly acid, and the process can be repeated several times in the cold before permanent neutralisation is attained. Acetylcarbinol is thus a pseudo-acid, and this conclusion has been confirmed by an examination of the electrical conductivities of solutions of acetylcarbinol in presence of sodium hydroxide. J. J. S.

Preparation of Thio-acids and Disulpho-acids. EINAR BILLMANN (*Annalen*, 1905, **339**, 351—372).—The non-crystalline thio-acids, which seem so far not to have been prepared in a pure state,

can be obtained by treating alkali salts of halogen-substituted fatty acids with potassium xanthate in aqueous solution, thus: $\text{OEt}\cdot\text{CS}_2\text{K} + \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{K} = \text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{K} + \text{KCl}$. On further treatment with ammonia, the xanthamides are formed, thus:



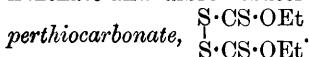
Xanthylacetic acid, $\text{C}_6\text{H}_8\text{O}_3\text{S}_2$, is prepared from potassium xanthate and sodium chloroacetate in aqueous solution; the mixture is kept overnight; since the xanthylacetic acid on heating in alkaline solution condenses to trithiocarbonylacetic acid, $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, it is necessary to cool with ice when preparing large quantities. The acid, which is a white, crystalline, odourless solid melting at $53-54^\circ$, forms hygroscopic alkali salts; the *lead* salt, $(\text{C}_6\text{H}_7\text{O}_3\text{S}_2)_2\text{Pb}\cdot\text{H}_2\text{O}$, is a micro-crystalline precipitate. On evaporating an alcoholic solution of the acid with ammonia, xanthamide is formed; the latter is converted by treatment with hydrogen chloride into thioglycollic acid, which is a colourless oil boiling at 123° under 29 mm. pressure; it forms an insoluble *barium* salt. *Disulphideacetic acid*, $\text{S}_2(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, prepared by oxidation of crude thioglycollic acid by means of iodine, melts at $107-108^\circ$ and gives a precipitate of silver sulphide with ammoniacal silver solution.

α -Xanthylpropionic acid, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared from sodium *α -bromopropionate* and potassium xanthate, is a colourless, crystalline substance melting at $49-50^\circ$; the alkali salts are hygroscopic, and the lead salt is unstable. *α -Disulphidepropionic acid*, $\text{S}_2(\text{CHMe}\cdot\text{CO}_2\text{H})_2$, forms white crystals melting at $140-142^\circ$. *β -Xanthylpropionic acid*, prepared from *β -iodopropionic acid*, forms crystals melting at 66° ; the *sodium* salt crystallises with $3\text{H}_2\text{O}$ in white, rectangular leaflets. *β -Disulphidepropionic acid* crystallises in white leaflets melting at 155° , and does not blacken with ammoniacal silver solution.

α -Xanthylbutyric acid, prepared from sodium *α -bromobutyrate* and potassium xanthate, forms white crystals melting at 55° . *α -Thiolbutyric acid*, $\text{SH}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$, is an oil boiling at $118-122^\circ$ under 19 mm. pressure; its basic *lead* salt is insoluble.

Xanthyleuccinic acid, $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}\cdot(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared from sodium bromosuccinate, crystallises in plates melting at 149° . Thiomalic acid forms crystals melting at 148° , and gives a characteristic reaction with copper sulphate.

Attempts to prepare thiotartaric acid lead to no result; potassium xanthate and dibromosuccinic acid give fumaric acid and *ethyl dioxy-*



K. J. P. O.

α -Alkylacrylic Acids. EDMOND E. BLAISE and A. LUTTRINGER (*Bull. Soc. chim.*, 1905, [iii], 33, 760-783. Compare this vol., i, 168).—The esters of *α -alkylacrylic acids* have been prepared by the action of phosphoric oxide on the esters of the corresponding hydroacrylic acids (this vol., i, 505). *Ethyl α -ethylacrylate*, $\text{CH}_2\cdot\text{Cet}\cdot\text{CO}_2\text{Et}$, is obtained together with *α -ethylacrylic acid*, tiglic acid, and the *ester*, $\text{CH}_2\cdot\text{Cet}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ (derived from *α -ethylacrylic acid* and *α -ethylhydracrylic acid*), by the action of phosphoric oxide on a benzene

solution of ethyl α -hydracrylate. The complex ester boils at $144\text{--}146^\circ$ under 24 mm. pressure, and when hydrolysed yields the two components, which were recognised by means of their reactions with phenylhydrazine at 140° . Ethyl α -ethylacrylate is a liquid distilling at 137° under atmospheric pressure, and the yield is some 65 per cent. The acid distils at 83° under 15 mm. pressure, melts at -16° , and dissolves only sparingly in water, but readily in organic solvents. The *potassium hydrogen salt*, $\text{KH}(\text{C}_5\text{H}_7\text{O}_2)_2$, and *ammonium salt* are both readily soluble in water. The *chloride*, $\text{CH}_2\text{:C}(\text{Et})\text{COCl}$, distils at 25° under 13 mm., or at 38.5° under 30 mm. pressure. The *amide* melts at 83.5° , the *anilide* at 82° , the *phenylhydrazide*, $\text{CH}_2\text{:C}(\text{Et})\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, at 77° , and the *dibromide*, $\alpha\beta$ -*dibromo- α -ethylpropionic acid*, obtained by the addition of bromine in carbon disulphide solution at 0° , crystallises from light petroleum and melts at 73° . β -*Bromo- α -ethylpropionic acid*, obtained by the addition of hydrogen bromide to the unsaturated acid, distils at $128\text{--}129^\circ$ under 15 mm. pressure, and its *ethyl ester* at $94\text{--}95^\circ$ under 20 mm. pressure. The corresponding *iodo-acid*, $\text{CH}_2\text{I}\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{H}$, crystallises from light petroleum, melts at 28° , and is extremely hygroscopic.

Ethyl α -ethylacrylate condenses with ethyl acetoacetate in the presence of sodium ethoxide at the ordinary temperature, yielding *ethyl α' -acetyl- α -ethylglutarate*, $\text{CO}_2\text{Et}\cdot\text{CHAc}\cdot\text{CH}_2\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{Et}$, which distils at 150° under 10 mm. pressure, and ethyl α -ethylglutarate (Auwers and Titherley, Abstr., 1896, i, 639). This latter is the only product when the condensation is effected by heating the mixture for six hours on the water-bath. When boiled with hydrochloric acid, the acetyethylglutarate is hydrolysed yielding carbon dioxide, ethyl alcohol, and γ -*acetyl- α -ethylbutyric acid*, $\text{CH}_3\text{Ac}\cdot\text{CH}_2\cdot\text{CH}(\text{Et})\cdot\text{CO}_2\text{H}$, which distils at 158° under 9 mm. pressure. The *semicarbazone* of the acid forms small crystals from a mixture of absolute ether and alcohol and melts at 125° .

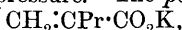
Aniline reacts with α -ethylacrylic acid at its boiling point, yielding the anilide of the acid together with β -*phenylamino- α -ethylpropion-anilide*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}(\text{Et})\cdot\text{CO}\cdot\text{NHPh}$, which crystallises in slender needles melting at 115° (compare Autenrieth and Pretzell, Abstr., 1903, i, 474).

α -Ethylacrylic acid condenses with phenylhydrazine, yielding 1-*phenyl-4-ethyl-5-pyrazolidone*, $\text{NPh}\begin{matrix} \text{CO}-\text{CH}(\text{Et}) \\ | \\ \text{NH}\cdot\text{CH}_2 \end{matrix}$, which melts at 79° and distils at $213\text{--}214^\circ$ under 15 mm. pressure. Its 2-*acetyl derivative*, $\text{NPh}\begin{matrix} \text{CO}-\text{CH}(\text{Et}) \\ | \\ \text{NAc}\cdot\text{CH}_2 \end{matrix}$, melts at $54\text{--}55^\circ$ and distils at $213\text{--}214^\circ$ under 28 mm. pressure. When heated with methyl iodide for six hours at 120° , the pyrazolidone yields the *compound*, $\text{NPh}\begin{matrix} \text{CO}-\text{CH}(\text{Et}) \\ | \\ \text{NHMeI}\cdot\text{CH}_2 \end{matrix}$, I_2 , melting at 126° , and when oxidised with potassium ferrieyanide it yields 1-*phenyl-4-ethyl-5-pyrazolone*, $\text{NPh}\begin{matrix} \text{CO}-\text{CH}(\text{Et}) \\ | \\ \text{N}=\text{CH} \end{matrix}$,

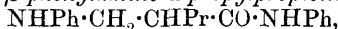
melting at 78° . α -Ethylacrylic acid and hydrazine hydrate react

yielding, among other products, a substance melting at 100° , distilling at about 300° , and containing 15.86 per cent. of nitrogen.

Ethyl α -propylacrylate (52 per cent. yield) distils at 156° under atmospheric pressure. The *acid* melts at -17° and distils at 101 – 102° under 15 mm. pressure. The *potassium* salt,

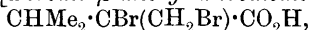


crystallises from alcohol in brilliant plates. The *acid*, when boiled with aniline, yields *β -phenylamino- α -propylpropionanilide*,



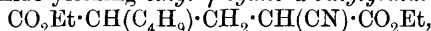
melting at 118.5° and soluble in hydrochloric acid.

Ethyl α -isopropylacrylate distils at 153° under the ordinary pressure, the *acid* at 100° under 19 mm. pressure, and its *dibromide*, *$\alpha\beta$ -dibromo- α -isopropylpropionic* [*α -bromo- β -methyl- α -bromomethylbutyric*] *acid*,

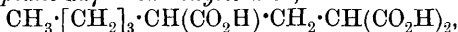


melts at 87° . *Ethyl α -butylacrylate* distils at 177° , the *acid* boils at 109 – 110° under 10 mm. pressure, and solidifies at -15° . The *potassium hydrogen*, *ammonium*, and *calcium* salts are all anhydrous, and the *cupric* salt crystallises with $5\text{H}_2\text{O}$. The *acid chloride* distils at 58 – 59° under 13 mm. pressure. The *anilide* melts at 41.5° , and the *phenylhydrazide* at 91.5° . The *acid* combines with hydrogen bromide, yielding *β -bromo- α -butylpropionic* [*α -bromomethylhexoic*] *acid*, which is an oil; its *ethyl* ester distils at 120 – 121° under 18 mm. pressure. *1-Phenyl-4-butyl-5-pyrazolidone* melts at 84° .

Ethyl α -butylacrylate and *ethyl cyanoacetate* condense in presence of sodium ethoxide yielding *ethyl γ -cyano- α -butylglutarate*,



which distils at 192° under 20 mm. pressure. When hydrolysed, the ester yields *heptane- $\alpha\gamma$ -tricarboxylic acid*,



which melts at 144° .

Ethyl α -heptylacrylate distils at 122° under 18 mm. pressure and the *acid* at 158° under the same pressure. The *potassium* salt crystallises from alcohol in plates.

J. J. S.

Preparation of Dimethylacrylic Acid. PHILIPPE BARBIER and GEORGES LÉSER (*Bull. Soc. chim.*, 1905, [iii], 33, 815–816).—The *acid* is readily prepared by adding pure mesityl oxide to a well-stirred solution of sodium hypochlorite, prepared by Graebe's method; the mixture becomes hot, and, when it has again attained the ordinary temperature, the excess of hypochlorite is destroyed by sodium hydrogen sulphite. The solution is decanted from the chloroform and acidified with sulphuric acid, when crystals of dimethylacrylic acid separate. A further quantity may be obtained by extracting the acid filtrate with ether. The yield is over 70 per cent.

J. J. S.

Crotonic and isoCrotonic Acids. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 254–255).—Crotonic and isocrotonic acids dissolved in glycerol were boiled for some time; in neither case was any gas evolved; the investigation is being continued.

P. H.

The Five Isomeric Acids, $C_4H_6O_2$. WILLHELM AUTENRIETH (*Ber.*, 1905, **38**, 2534—2551).—The five acids of the formula $C_4H_6O_2$, $\begin{array}{c} H \cdot C \cdot Me \\ | \\ H \cdot C \cdot CO_2H \end{array}$, $\begin{array}{c} Me \cdot C \cdot H \\ | \\ H \cdot C \cdot CO_2H \end{array}$, $CH_2 \cdot CMe \cdot CO_2H$,

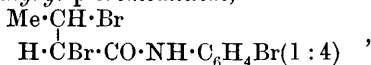
$CH_2 \cdot CH \cdot CH_2 \cdot CO_2H$, and $CH_2 \cdot \begin{array}{c} CH_2 \\ | \\ CH \cdot CO_2H \end{array}$, are now known as uniform individuals. That four of these acids contain an ethylenic linking is shown by the fact that the anilides obtained from them unite with two atoms of bromine or one molecule of aniline to form saturated compounds. The fifth acid, trimethylenecarboxylic acid, is saturated, its anilide yielding a monobromo-substitution product.

β -Chlorocrotonic and β -chloroisocrotonic acids are $\alpha\beta$ -unsaturated acids and are structurally identical, just as are crotonic and isocrotonic acids. The mercaptol esters of ethyl acetoacetate of the general type $CMe(SR)_2 \cdot CH_2 \cdot CO_2Et$, and the disulphonyl esters of the type $CMe(SO_2R)_2 \cdot CH_2 \cdot CO_2Et$, give, with alkalis, derivatives of isocrotonic acid. Further, with phenylhydrazine, ethyl β -chloroisocrotonate forms phenylmethylpyrazolone and other pyrazolone derivatives, containing a methyl group.

Since the tribromide, obtained by the action of bromine on isocrotonanilide, yields α -bromocrotonic acid only on hydrolytic decomposition by hydrochloric acid, the constitution of isocrotonic acid is regarded as definitely settled.

[With CARL PRETZELL.]—*isoCrotonanilide*, $\begin{array}{c} Me \cdot C \cdot H \\ | \\ H \cdot C \cdot CO \cdot NHPh \end{array}$, prepared by the action of aniline on isocrotonic chloride, crystallises in prisms and melts at 102° .

iso- $\alpha\beta$ -Dibromobutyryl- p -bromoanilide,



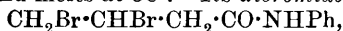
prepared by the action of a solution of bromine in chloroform on isocrotonanilide, forms glistening prisms and melts at 146° . When heated with fuming hydrochloric acid at 120 — 130° for six hours, it forms α -bromocrotonic acid, melting at 106° , and p -bromoaniline.

Benzoyl- p -bromoanilide, prepared from p -bromoaniline by the Schotten-Baumann method, separates from alcohol in glistening, hexagonal plates and melts at 202° .

$\alpha\beta$ -Dibromobutyryl- p -bromoanilide, $\begin{array}{c} H \cdot CBrMe \\ | \\ H \cdot CBr \cdot CO \cdot NH \cdot C_6H_4Br \end{array}$, prepared

by the action of bromine (2 atoms) on $\alpha\beta$ -dibromobutyranilide or by the action of bromine (4 atoms) on crotonanilide, both reactions having been conducted in chloroform solution, separates from alcohol in glistening leaflets and melts at 154 — 155° . By its hydrolytic decomposition with hydrochloric acid at 130° , p -bromoaniline, hydrobromic acid, and a bromocrotonic acid (m. p. 97°) were obtained, the latter being probably identical with the acid designated in the literature as β -bromocrotonic acid.

Vinylacetanilide, $CH_2 \cdot CH \cdot CH_2 \cdot CO \cdot NHPh$, separates from dilute alcohol in needles and melts at 58° . Its *dibromide*,

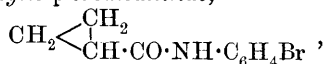


prepared by the action of bromine on a solution of the anilide in chloroform, crystallises in needles and melts at 101° .

Methylacrylanilide dibromide, $\text{CH}_2\text{Br}\cdot\text{CBrMe}\cdot\text{CO}\cdot\text{NHPh}$, prepared by the action of bromine on a chloroform solution of methylacrylanilide, separates from alcohol in needles and melts at 128° .

Trimethylenecarboxylic anilide, $\text{CH}_2\begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{CH}\cdot\text{CO}\cdot\text{NHPh} \end{smallmatrix}$, prepared by the addition of aniline to trimethylenecarboxylic chloride, separates from water or dilute alcohol in glistening leaflets and melts at $110\text{--}111^{\circ}$.

Trimethylenecarboxylic p-bromoanilide,



prepared by the bromination of the preceding compound, separates from alcohol in glistening prisms and melts at $189\text{--}190^{\circ}$.

Its constitution was determined by its behaviour on hydrolysis with fuming hydrochloric acid at 120° , when *p*-bromoaniline and an acid which did not contain bromine (probably trimethylenecarboxylic acid) were obtained.

A. MCK.

d-Lactide. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1905, 141, 111—113. Compare Wislicenus, *Abstr.*, 1873, 57).—If small quantities of *d*-lactic acid are heated at about 70° under 25 mm. pressure to complete elimination of water, and the product rapidly distilled at $150\text{--}155^{\circ}$, the distillate contains *d*-lactide only; but if large quantities of acid are distilled, the heating must be prolonged and the distillate contains *d*- and *i*-lactides, which can be separated by fractional crystallisation.

i-Lactide forms triclinic crystals, whilst those of the *d*-modification are orthorhombic. *d*-Lactide melts at 95° , distils at 150° under 25 mm. pressure, is highly hygroscopic, and is more soluble than the *i*-modification in ether, alcohol, chloroform, or benzene. The value of $[\alpha]_D$ for *d*-lactic acid decreases with dilution; solutions containing 1.1665, 0.5832, and 0.2916 gram of $\text{C}_6\text{H}_8\text{O}_4$ per 100 c.c. of benzene have $[\alpha]_D - 298^{\circ}$, -280° , and -246° respectively at 18° . In contact with water, *d*-lactide dissolves more rapidly than does the *i*-modification, the solution becoming acid and less laevorotatory owing to formation of *d*-lactyl-lactic acid, which is gradually partially hydrolysed into *d*-lactic acid, with which it forms an equilibrium in aqueous solution. Thus a solution of 0.117 gram of *d*-lactide in 30 c.c. of water immediately after formation and after 2, 6, 12, 48, and 72 hours has $[\alpha]_D - 192.8^{\circ}$, -141° , -111° , -59.8° , -42.7° , and -8° respectively at 13° . Similar changes take place, but more rapidly, at 100° . A concentrated solution of laevorotatory zinc *d*-lactyl-lactate is obtained by neutralising the freshly prepared aqueous solution of *d*-lactide with zinc carbonate and evaporating at low temperatures; this unstable salt could not be obtained in the crystalline state, as after some time in the cold, or more rapidly on boiling, the solution deposits zinc *d*-lactate, which is only slightly laevorotatory, and becomes acid owing to the formation of free *d*-lactic acid. Thus a solution of zinc *d*-lactyl-

lactate which had $[\alpha]_D -7.5^\circ$, after some hours of boiling had $[\alpha]_D -0.3^\circ$. G. Y.

$\beta\beta$ -Dimethylbutyrolactone. GUSTAVE BLANC (*Compt. rend.*, 1905, 141, 203—204) —Blaise's supposed $\beta\beta$ -dimethylbutyrolactone (Abstr., 1898, i, 561) must be a mixture of that substance with the $\alpha\alpha$ -dimethyl-compound, as the ethyl γ -bromodimethylbutyrate obtained from it boils at $102-104^\circ$ under 9 mm. pressure, and when treated with ethyl sodiocyanoacetate yields only a small amount of ethyl cyano- $\alpha\alpha$ -dimethyladipate, which boils at 175° under 8 mm. pressure and on hydrolysis is converted into $\alpha\alpha$ -dimethyladipic acid melting at 87° , whilst the action of ethyl sodiocyanoacetate on the α -bromo-ester from $\beta\beta$ -dimethylbutyrolactone leads to the elimination of hydrogen bromide and the formation of the ester, $C_5H_9\cdot CO_2Et$. G. Y.

Ethyl Dicyanosuccinate. P. ENGLER and JULIUS MEYER (*Ber.*, 1905, 38, 2486—2488).—When shaken with iodine in ethereal solution, ethyl sodiocyanoacetate yields *ethyl dicyanosuccinate*, $C_{10}H_{12}O_4N_2$, which crystallises in white leaflets, melts at 118° , and is insoluble and comparatively stable in cold water, but is easily hydrolysed by boiling water or aqueous alkali hydroxides, carbonates, or thiosulphates. The product of hydrolysis is probably diethyl dihydrogen ethanetetracarboxylate; the silver salt could not be obtained in a state of purity.

The action of iodine on a mixture of ethyl sodiomalonate and ethyl sodiocyanoacetate leads chiefly to the formation of ethyl ethane-tetracarboxylate. G. Y.

Derivatives of Dibromo- and Dichloro-maleic Acid and their Conversion into Indigo. ALFRED SALMONY and HUGO SIMONIS (*Ber.*, 1905, 38, 2580—2601. Compare Abstr., 1901, i, 268).—Good yields of dibromo- and dichloro-maleic acids may be obtained by oxidising mucobromic and mucochloric acids (Abstr., 1899, i, 741) by Hendrixon's method (Abstr., 1890, 958).

The following salts of dibromomaleic acid have been prepared: *potassium* ($1H_2O$), *sodium potassium*, *cobalt* ($2H_2O$).

Ethyl hydrogen dibromomaleate, obtained by the half esterification of the acid, forms a solid mass melting at 100° and decomposing into the anhydride and alcohol when heated. The *propyl hydrogen* ester and the *amyl hydrogen* ester are oils, and their stability increases with the complexity of the alkyl group present. The normal methyl ester (Abstr., 1888, 1058) is best obtained by the hydrogen chloride catalytic method. The normal *allyl* ester and the corresponding *tert.-butyl* ester are oils. The *isoamyl* ester distils at 320° . In the preparation of the esters from the silver salts and alkyl iodides, it is essential that no free iodine should be present, as this readily transforms the maleates into the corresponding fumarates.

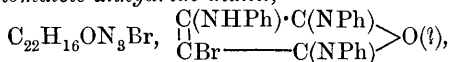
The following salts and esters of dichloromaleic acid have been prepared: *potassium* (H_2O), *sodium* (H_2O), *sodium hydrogen* (H_2O), *lithium*, *cupric* (H_2O), *plumbous* (H_2O), *nickelous* ($2H_2O$). The *isobutyl hydrogen* ester distils at $168-170^\circ$, but is partially decomposed. *Aniline dibromomaleate*, $C_2Br_2(CO_2NH_3Ph)_2$, obtained when cold alcoholic solutions of the components are mixed, crystallises in soft, glistening, white scales. It begins to decompose at 128° , dissolves

readily in water, and only sparingly in most organic solvents with the exception of carbon disulphide. The *o*-toluidine salt crystallises in needles melting at 139°, and the *p*-compound in plates decomposing at 154°. *Aniline dichloromaleate* begins to decompose at 125°.

When aniline and the dibromo-acid are boiled with water and a little ether and the solution subsequently evaporated, a mixture of two isomeric *anilinobromomaleic anhydride anils* is obtained. The one, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{||} \\ \text{C(NPh)} \end{smallmatrix} \text{CO} \begin{smallmatrix} \text{||} \\ \text{CBr} \end{smallmatrix} \text{CO} > \text{O}$, crystallises from 90 per cent. alcohol in yellowish-green needles, melts at 180°, and dissolves in potassium hydroxide solution. The second, $\text{C} \begin{smallmatrix} \text{||} \\ \text{C(NHPh)} \end{smallmatrix} \text{CO} \begin{smallmatrix} \text{||} \\ \text{CBr} \end{smallmatrix} \text{C(NPh)} > \text{O}$, crystallises from water in slender, brown needles melting at 188°; it dissolves in potassium hydroxide, and on the addition of hydrochloric acid to the solution copious evolution of carbon dioxide ensues. A third *isomeride*, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{||} \\ \text{CBr} \end{smallmatrix} \text{CO} \begin{smallmatrix} \text{||} \\ \text{CBr} \end{smallmatrix} \text{CO} > \text{NPh}$, is obtained by the action of aniline on dibromomaleic anhydride; it forms orange-yellow plates, melts at 192°, is readily soluble in hot alcohol or ether, and may be sublimed.

Anilinobromomaleic anhydride, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{||} \\ \text{CBr} \end{smallmatrix} \text{CO} \begin{smallmatrix} \text{||} \\ \text{CBr} \end{smallmatrix} \text{CO} > \text{O}$, crystallises from alcohol in golden-yellow needles. The three *chloro*-derivatives corresponding with the isomeric anilinobromo-anils have been prepared. The first turns brown at 175°, and melts at 188°, the second crystallises in golden plates and melts at 187°, and the third in prismatic, orange-red needles melting at 190°. *Anilinochloromaleic anhydride* is readily soluble in most organic solvents and begins to melt at 165°.

Anilinobromomaleic anhydride dianil,



obtained as a by-product in the preparation of methyl dianilinomaleate, crystallises from alcohol in orange-red plates melting at 186°.

A *trianilinobromodimaleic anhydride dianil*, $\text{C}_{38}\text{H}_{38}\text{O}_4\text{N}_5\text{Br}$, is obtained as a by-product in the preparation of dianilinomaleic anhydride. It has a brownish-red colour, dissolves readily in alcohol, melts at 160°, and does not crystallise well. The corresponding *chloro*-derivative turns black at 120°.

It has not been found possible to replace both bromine atoms in dibromomaleic acid by anilino-groups, but the change may be effected, although not readily, in the case of the anhydride or methyl ester.

Dianilinomaleic anhydride, $\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{||} \\ \text{C} \end{smallmatrix} \text{CO} \begin{smallmatrix} \text{||} \\ \text{C} \end{smallmatrix} \text{CO} > \text{O}$, formed by adding

aniline at 100–120° to dibromomaleic anhydride and subsequently heating at 130–140°, crystallises from boiling alcohol and melts at 231°.

Methyl dianilinomaleate crystallises in yellow prisms and melts at 172°, the *acid* assumes an orange colour at 140°, melts, and again solidifies, and then melts and decomposes at 175°. The *sodium* and *silver* salts were prepared.

When the methyl ester is fused with caustic potash, or when the sodium salt is fused with pure sodamide and a little potassium hydroxide, small amounts of indigo are obtained. J. J. S.

Preparation of Carbon Compounds containing Two Consecutive Double Linkings. ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 568—576).—The author describes unsuccessful attempts to synthesise compounds of the allene type, which have been but little studied and should prove of stereochemical interest.

Starting from ethyl diethylacetonedicarboxylate, he converted this, by the action of phosphorus pentachloride, into ethyl chlorodiethylglutaconate, $\text{CO}_2\text{Et}\cdot\text{CHEt}\cdot\text{CCl}\cdot\text{CEt}\cdot\text{CO}_2\text{Et}$. All the means adopted for the removal of hydrogen chloride from the last compound led also to simultaneous substitution by hydroxyl. The action of alcoholic potassium hydroxide yielded ethylmalonic acid, butyric acid, and dipropyl ketone, whilst hydrochloric acid, acetates, and solutions of potassium hydroxide in water or methyl alcohol gave mixtures of the ethyl esters of chlorodiethylglutaconic and diethylacetonedicarboxylic acids and a certain amount of resin. Similar results were obtained with ethyl iododiethylglutaconate. T. H. P.

Solubility of Certain Metallic Tartrates in Water. H. CANTONI and Mlle. F. ZACHODER (*Bull. Soc. chim.*, 1905, [iii], 33, 747—754. Compare this vol., i, 14).—The solubilities of the tartrates of strontium, calcium, barium, copper, zinc, and lead have been determined at various temperatures between 0° and 85° , and the results are given in tables and curves in the original. J. J. S.

Formaldehyde and Formate Formation. HANS EULER and ASTRID EULER (*Ber.*, 1905, 38, 2551—2560).—The authors have studied the condition of formaldehyde in dilute alkaline solution. Formaldehyde behaves as a weak acid since, by the action of formaldehyde on alkali, the alkali salt of the aldehyde is formed, and this is partially hydrolysed in aqueous solution. A $N/1$ solution of the monosodium salt of formaldehyde contains about one-half of the salt as such, whilst the other half is resolved into free base and free formaldehyde. In dilute solution, the salt is a binary electrolyte; the strength (dissociation constant) of formaldehyde as an acid amounts to $1\cdot10^{-14}$ at 0° .

The formation of sodium or barium formate from formaldehyde and sodium hydroxide is a reaction of the second order. With a large excess of aldehyde, the reaction is one of the first order. The value of the constant falls slightly with the time. The reaction constants for barium hydroxide or sodium hydroxide are about the same, and fall somewhat with increase of the initial concentration of the aldehyde on account of the formation of the formaldehyde salt. In the formate formation examined, no oxidation occurred, since the reaction took place as quickly in an atmosphere of hydrogen as in oxygen. The reaction constant is tripled with a rise of temperature of 10° . Formate formation takes place more quickly with calcium hydroxide than with sodium or barium hydroxide.

A. McK.

Crystals of *s*-Tetrachloroisopropyl Formal. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1905, 211—213).—Polemical. A reply to Cesàro (this vol., i, 570). P. H.

Dichloroacetyldextrin. A. KLDIASCHWILI (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 421—423).—*Dichloroacetyldextrin*, $C_8H_{10}O_6Cl_2$, is obtained by mixing rice starch with twice its weight of dichloroacetic acid in the cold and heating the whole in a reflux apparatus until the product gives no starch reaction with iodine even after saponification. It is deposited from acetone in a powdery mass, and ebullioscopic measurements of its solution in this solvent indicate a molecular weight corresponding with $6C_8H_{10}O_6Cl_2$. T. H. P.

Action of Ethylamine and *iso*Butylamine on Cæsium. ETIENNE RENGADÉ (*Compt. rend.*, 1905, 141, 196—198. Compare this vol., i, 174).—Cæsium dissolves in ethylamine to form an unstable, blue *cæsium-ethylammonium*, which decomposes into hydrogen and *cæsium-ethylamide*, NH_2EtCs ; this crystallises in long, white needles, becomes yellow on exposure to air, inflames explosively when rapidly heated or on contact with moist air, and dissolves easily in ethylamine. It reacts with aqueous vapour in a vacuum to form ethylamine and cæsium hydroxide, and when slowly heated to 105—110° decomposes with formation of hydrogen, methane, and ethylene.

Cæsium dissolves in *isobutylamine* to form a colourless solution which yields hydrogen and, on evaporation of the excess of the base, *cæsium isobutylamide*, C_4H_9NHCs , which crystallises in white needles, is more stable than the methyl- or ethylamine compounds, becomes brown and inflames, but without detonation on contact with moist air, reacts with water in absence of air to form *isobutylamine* and cæsium hydroxide, and when heated to 110° undergoes a complex decomposition, with evolution of hydrogen, and finally of propane and propylene.

Cæsium-ethylamide is formed when cæsium-amide is dissolved in ethylamine and the solution evaporated; similarly, cæsium-ethylamine is converted into the amide and the *isobutylamide* by treatment with excess of ammonia and *isobutylamine* respectively. If a limited quantity of the ammonia or amine is used as solvent, an equilibrium is set up between the two possible amides and the two amines or the amine and ammonia. G. Y.

New Method for the Conversion of Primary Diamines into Chlorinated Amines and into Dichlorides. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1905, 38, 2340—2348).—A 60 per cent. yield of α -dichloropentane, together with benzonitrile, is obtained by heating dibenzoylpentamethylenediamine with phosphorus pentachloride and distilling under atmospheric pressure. The product is distilled in steam, the nitrile hydrolysed with concentrated hydrochloric acid and the mixture again distilled in steam, when the dichloropentane passes over.

If the product is distilled under reduced pressure, a certain amount of benzoyl ϵ -chloroamylamine is obtained, and this, on hydrolysis, yields ϵ -chloroamylamine.

Other dichlorides and chloroamines may be obtained in a similar manner. A 60 per cent. yield of $\alpha\zeta$ -dichlorohexane has been obtained from hexamethylenediamine. ζ -Chlorohexylamine, $\text{NH}_2 \cdot [\text{CH}_2]_6 \cdot \text{Cl}$, is an oil, and the *hydrochloride* a syrup; the *platinichloride* melts at $213\text{--}214^\circ$ and the *picrate* at 115° . An aqueous suspension of the base gradually loses its alkaline properties when heated, as intramolecular transformations occur, one of the products being hexamethyleneimine, $(\text{CH}_2)_6 \cdot \text{NH}$. The best yield of the chlorinated base is obtained by reducing ϵ -phenoxyhexonitrile (this vol., i, 342) and replacing the phenoxy-group by chlorine.

$\alpha\eta$ -Dichloroheptane distils at 120° under 28 mm. pressure, and with sodium phenoxide yields $\alpha\eta$ -diphenoxyheptane melting at 53° (Solonina, Abstr., 1899, i, 561). Benzoyl- η -chloroheptylamine forms a snow-white, crystalline powder melting at 63° , and when hydrolysed with concentrated hydrochloric acid at 150° yields η -chloroheptylamine *hydrochloride* as a syrup. The *platinichloride* melts at 203° . The base is an oil with alkaline properties, and when heated with water undergoes intramolecular rearrangement.

J. J. S.

Reduction of Ketoximes. New Synthesis of Amines.

AMABLE MAILHE (*Compt. rend.*, 1905, **141**, 113—115. Compare this vol., i, 571).—When heated with finely-divided nickel at $150\text{--}180^\circ$, acetoxime yields a liquid which consists to the extent of about $1/3$ of isopropylamine and of $2/3$ of diisopropylamine. There is obtained also a small quantity of a liquid boiling at about 105° which is probably a mixture of di- and tri-isopropylamine.

Methyl ethyl ketoxime is reduced by finely-divided nickel at $150\text{--}200^\circ$, about $1/3$ of the product being *sec*-butylamine, and about $2/3$ di-*sec*-butylamine, with a small quantity of a liquid boiling below 160° and containing probably tri-*sec*-butylamine. Methyl ethyl ketoxime is reduced by nickel at 250° to ammonia, butane, and water, whilst with finely divided copper at 300° it forms the primary and secondary amines.

Di-*sec*-butylamine is a colourless liquid of characteristic odour, which boils at 132° under 758 mm. pressure, has a sp. gr. 0.7833 at 0° , and is extremely soluble in water. The *hydrochloride* is deliquescent; the *oxalate* melts at 104° .

The *hydrochloride* and *carbonate* of *sec*-butylamine crystallise in slender needles and are deliquescent.

Methyl *n*-propyl ketoxime is reduced by finely-divided nickel at $180\text{--}200^\circ$, $2/5$ of the product being *sec*-amylamine and $3/5$ di-*sec*-amylamine; at 250° , the reduction leads to the formation of ammonia, water, and the hydrocarbon. The primary and secondary amines are also formed by reduction by means of finely-divided copper. *sec*-Amylamine reacts with phenylcarbimide to form *s*-phenyl-*sec*-amyl-carbamide, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMePr}^a$, which crystallises in prisms and melts at 120° .

Di-*sec*-amylamine, $\text{NH}(\text{CHMePr}^a)_2$, boils at 177° under 750 mm. pressure, has a sp. gr. 0.7916 at 0° , forms a deliquescent *hydrochloride*, and reacts with phenylcarbimide to form *a*-phenyl-bb-di-*sec*-amylcarb-

amide, $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{CHMePr}^a)_2$, which crystallises in needles and melts at 134° . G. Y.

Synthesis of Hexamethylenediamine and Heptamethylenediamine from Piperidine. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1905, 38, 2203—2210).—Benzoyl- ϵ -leucinonitrile,



prepared from benzoyl- ϵ -chloroamylamine, $\text{NHBz}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\text{Cl}$ (Abstr., 1904, i, 918), gives on reduction with sodium and absolute alcohol an oil consisting of a mixture of the monobenzoyl derivative, $\text{NHBz}\cdot[\text{CH}_2]_6\cdot\text{NH}_2$, of hexamethylenediamine with some of the base produced by hydrolysis; the oil is converted by benzoylchloride into dibenzoylhexamethylenediamine ($\alpha\zeta$ -dibenzoyldiaminohexane, Curtius and Clemm, Abstr., 1901, i, 68), $\text{NHBz}\cdot[\text{CH}_2]_6\cdot\text{NHBz}$, which crystallises from alcohol. On heating the dibenzoyl derivative with concentrated hydrochloric acid, $\alpha\zeta$ -diaminohexane hydrochloride, identical with Curtius and Clemm's product, is obtained. The *benzenesulphonic* derivative, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot[\text{CH}_2]_6\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$, crystallises from alcohol and melts at 154° .

Pimelonitrile (Abstr., 1904, i, 970) is easily reduced by sodium and absolute alcohol, giving heptamethylenediamine, $\text{NH}_2\cdot[\text{CH}_2]_7\cdot\text{NH}_2$, identical with Solonina's product (*J. Russ. Phys. Chem. Soc.*, 1896, 28, 558), prepared from suberic acid. The *benzenesulphonic* derivative, $\text{NHBz}\cdot[\text{CH}_2]_7\cdot\text{NHBz}$, crystallises from methyl alcohol on adding ether and melts at 104° . In the formation of heptamethylenediamine from pimelonitrile, an imino-base, $[\text{CH}_2]_7>\text{NH}$, is not formed, although the reduction of dicyanoethane or $\alpha\gamma$ -dicyanopropane gives rise to a cyclic imine as well as the aliphatic base. The tendency to form the imino-compound seems to cease when the carbon chain becomes 5-membered.

W. A. D.

Synthesis of a New Leucine. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1905, 141, 115—117. Compare this vol., i, 32, 33; Ehrlich, Abstr., 1904, i, 560).—Two alcohols are formed by the fermentation of beet-root juice: *isobutylcarbinol*, related to leucine, and *sec-butylcarbinol*, related presumably in a similar manner to Ehrlich's *d-isoleucine*, which must therefore have the constitution $\text{CHMeEt}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$. An inactive leucine of this constitution has been prepared in the following manner.

Ethyl sec-butylacetoacetate, $\text{CHMeEt}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, formed by the action of *sec-butyl* iodide on ethyl sodioacetoacetate, is a colourless liquid which boils at 111 — 112° under 19 mm. pressure, has a sp. gr. 0.976 at $4^\circ/0^\circ$, and with hydrazine forms a *pyrazolone* melting at 162° (corr.). When treated with nitrosyl sulphate in sulphuric acid solution, ethyl *sec-butylacetoacetate* yields *ethyl α -oximino-sec-butylacetate* [α -oximino- β -methylvalerate], $\text{CHMeEt}\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{Et}$, which is a viscid liquid boiling at 133 — 134° under 10 mm. pressure, and is easily hydrolysed by aqueous potassium hydroxide; the acid melts, decomposes, and sublimes at 164° (corr.). Along with the oximino-ester, there is formed a small quantity of *ethyl methylethylpyruvate*, which

yields a *semicarbazone* melting at 80—82°; the *acid* melts at 212° (corr.).

α -Amino-*sec*-butylacetic [α -amino- β -methylvaleric] *acid* is formed in a poor yield by reduction of ethyl α -oximino-*sec*-butylacetate with sodium amalgam. It is characterised by conversion into the *p*-toluene-sulphonate, which melts at 141° (corr.). A 60 per cent. yield of the *ester*, $\text{CHMeEt}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{Et}$, is obtained by reduction of the oximino-*ester* with sodium amalgam in cooled alcoholic solution, neutralised from time to time by addition of alcoholic hydrochloric acid. It is a colourless liquid with a disagreeable odour, which boils at 90—92° under 15 mm. pressure and has a sp. gr. 0.957 at 4°/0°. With potassium cyanate in hydrochloric acid solution, it yields the crystalline *carbamido*-derivative, $\text{CHMeEt}\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CO}_2\text{Et}$, which melts at 81°. With benzoyl chloride in cooled pyridine solution, the amino-*ester* forms an oily *benzoyl* derivative, which boils at 213—214° under 19 mm. pressure, and is hydrolysed by alcoholic potassium hydroxide with formation of α -benzoylamino- β -methylvaleric acid, $\text{CHMeEt}\cdot\text{CH}(\text{NHBz})\cdot\text{CO}_2\text{H}$, which sinters at 115° and melts at 118°. The corresponding benzoyl derivative of Ehrlich's *d*-isoleucine sinters at 114° and melts at 116—117° (Abstr., 1903, i, 796).

G. Y.

Synthesis of Polypeptides. XII. Alanylalanine and its Derivatives. EMIL FISCHER and KARL KAUTZSCH (*Ber.*, 1905, 38, 2375—2385. Compare Abstr., 1903, i, 465, 607, 799, 800; 1904, i, 652, 771, 867, 890, 917; this vol., i, 30, 31, 263).—Alanylalanine, $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is obtained by shaking alanine anhydride for some time with sodium hydroxide until the crystals which are first formed redissolve. The alkaline solution is neutralised with hydriodic acid, as the sodium iodide thus formed is readily soluble and the dipeptide practically insoluble in absolute alcohol. It crystallises from dilute alcohol in small needles, and melts and decomposes at 276° (corr.), its aqueous solution reacts feebly acid and dissolves cupric oxide, yielding a deep blue solution of the *cupric* salt, which is readily soluble in water and also moderately in alcohol.

Benzoylalanylalanine, $\text{CPh}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, crystallises from water in colourless needles and melts at 203—204° (corr.). The *copper* salt, $(\text{C}_{13}\text{H}_{15}\text{O}_4\text{N}_2)_2\text{Cu}$, crystallises in microscopic, green needles, which seem to contain water of crystallisation. The *ethyl ester* melts at 114—116° (corr.). These products are probably stereoisomeric with those described by Curtius and van der Linden (Abstr., 1904, i, 883).

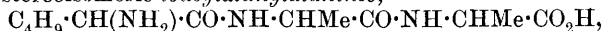
α -Bromoisohexoylalanylalanine,



is obtained by the action of α -bromoisohexoyl chloride on an alkaline solution of alanine anhydride in two stereoisomeric modifications, which may be separated by repeated fractional crystallisation from ethyl acetate. The A compound, which is less readily soluble, crystallises in slender needles, softens at 180°, melts and decomposes at 191—193° (corr.), and dissolves readily in hot alcohol or acetic acid. One gram dissolves in about 80 c.c. of hot water or 35 c.c. of hot

ethyl acetate. The B compound melts at 160—163° and decomposes at a slightly higher temperature. One gram dissolves in 25 c.c. of boiling water or in 6 c.c. of boiling ethyl acetate.

Two stereoisomeric *leucylalanylanines*,



are obtained by the action of ammonia on the bromo-derivatives at 100°. The A compound sinters at 240° and melts and decomposes at 266° (corr.). It dissolves in hot water, dilute acids, or acetic acid, but is practically insoluble in the usual organic solvents. It gives a violet coloration with sodium hydroxide and cupric sulphate solutions. The *copper* salt has been obtained in the amorphous condition only. The B compound is amorphous, dissolves readily in water, and is not precipitated by alcohol. The *methyl ester* and *copper* salt are also amorphous.

α-Bromopropionylalanylanine also exists in two modifications; the A compound, obtained by repeated crystallisation from water, melts and decomposes at 198—200° (corr.), dissolves sparingly in cold water, and moderately in hot ethyl acetate, acetone, or acetic acid. The B compound has not been obtained pure.

Dialanylanine, $\text{NH}_2\cdot[\text{CHMe}\cdot\text{CO}\cdot\text{NH}]_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, crystallises in needles, melts and decomposes at 219° (corr.) when quickly heated, then solidifies, and melts and decomposes again at 256—261° (corr.). It dissolves readily in cold water, sparingly in alcohol, contains $\frac{1}{2}\text{H}_2\text{O}$, which it loses at 100°, and then forms a hygroscopic powder. It is tasteless and yields an amorphous *cupric* salt. J. J. S.

Chromous Sodium Thiocyanate. IWAN KOPPEL (*Zeit. anorg. Chem.*, 1905, 45, 359—361).—When moist chromium acetate is gradually added, in absence of air, to a concentrated solution of sodium thiocyanate, it dissolves at first with production of a deep blue colour, and later a large yield of dark blue crystals having the composition $3\text{NaCNS}\cdot\text{Cr}(\text{CNS})_2\cdot 11\text{H}_2\text{O}$ separates. The crystals are easily decomposed by the action of oxygen or moisture.

The preparation of chromous chloride by the action of hydrochloric acid on small lumps of metallic chromium is recommended; the chromium is best prepared by the Goldschmidt aluminium process. Chromous chloride is thus obtained as a white, anhydrous product.

D. H. J.

Bromodialkylacetamides. KALLE & Co. (D.R.-P. 158220).—Bromodialkylacetamides of the formula $\text{CBrRR}'\cdot\text{CO}\cdot\text{NH}_2$ or $\text{CBrRR}'\cdot\text{C}(\text{OH})\cdot\text{NH}$ have a hypnotic action when R and R' = Et or Pr. Bromodimethylacetamide (*α-bromoisobutyramide*, Abstr., 1898, i, 10) has no such action.

To prepare these derivatives, the corresponding dialkylacetic acids are converted into the chlorides or bromides by phosphorus chloride or phosphorus and bromine respectively, and the amides prepared by passing ammonia into the ethereal solution or by adding to an excess of ammonia solution.

α-Bromo-α-ethylbutyryl chloride, $\text{CBrEt}_2\cdot\text{COCl}$, boils at 90—100° under 20 mm. pressure; *α-bromo-α-ethylbutyramide* melts at 64—65°

and dissolves in 115 parts of cold water, readily in alcohol, ether, benzene, or chloroform. *α*-Bromo-*α*-propylvaleryl chloride, $\text{CBrPr}_2\cdot\text{COCl}$, boils at $110\text{--}130^\circ$ under 20 mm. pressure; the *amide* melts at $59\text{--}60^\circ$ and is less soluble in water than the diethyl derivative. *α*-Bromo-*α*-ethylvaleramide is a pleasant-smelling oil. C. H. D.

isoCarbamides. JULIUS STIEGLITZ and R. W. NOBLE (*Ber.*, 1905, 38, 2243—2244. Compare Stieglitz and McKee, *Abstr.*, 1899, i, 594; 1900, i, 340, 431).—*O*-Alkyl esters of *isocarbamide* are readily prepared by warming cyanamide monohydrochloride (a mixture of cyanamide and cyanamide dihydrochloride) with a slight excess of the appropriate alcohol at about $60\text{--}70^\circ$.

O-Ethylisocarbamide hydrochloride (ethyl iminocarbamate hydrochloride), $\text{NH}_2\cdot\text{C}(\text{OEt})\text{:NH}\cdot\text{HCl}$, forms well-defined crystals and gives a *platinichloride*, $\text{C}_6\text{H}_{18}\text{O}_2\text{N}_4\text{PtCl}_6$.

O-Propylisocarbamide hydrochloride (propyl iminocarbamate hydrochloride) melts at 64° and decomposes at 121° . W. A. D.

Dimethylmethylenetrimethylene, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C}:\text{CMe}_2$. D. W.

ALEXÉEFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 417—421).—*Dimethyl-*

methylenetrimethylene [β -propylenecyclopropane], $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C}:\text{CMe}_2$, pre-

pared by heating cyclopropyldimethylcarbinol in a sealed tube with acetic anhydride, has the odour of the naphthalene hydrocarbons, boils at $70.5\text{--}71^\circ$ under 763 mm. pressure, has the sp. gr. 0.7532 at $20^\circ/0^\circ$, and n_D 1.424. When the hydrocarbon is treated in the dark with a chloroform or carbon disulphide solution of bromine, two atoms of the latter are taken to satisfy the double linking and two more owing to the rupture of the carbon ring, while still more of the bromine brings about bromination accompanied by evolution of hydrogen bromide. T. H. P.

Purification of *o*-Nitrotoluene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158219. Compare Streng, *Abstr.*, 1891, 1197; Schneider, *Abstr.*, 1896, ii, 290).—*o*-Nitrotoluene freezes at -10.5° , but if cooled to -4° , crystals are obtained differing in form from those separating at -10.5° . It is thus possible to purify *o*-nitrotoluene by cooling the crude product to temperatures between -4° and -10° and removing the liquid portion by centrifugalisation when about one-half has crystallised. A mixture of *o*-nitrotoluene with 6 per cent. of *p*-nitrotoluene and 12 per cent. of *m*-nitrotoluene begins to crystallise at -9° . C. H. D.

Nitration of Aromatic Arylsulphonamides. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 157859).—It is not practicable to nitrate arylsulphonamides in sulphuric acid solution, but the reaction takes place smoothly when the amides are suspended in water and gently warmed with dilute nitric acid. The nitro-group always enters the para-position to the sulphonamide group, and secondary reactions do not occur.

The arylsulphonamides of benzene and toluene, derived from primary and secondary aromatic bases, are almost insoluble in water, but dissolve readily in alcohol, ether, or benzene. Those derived from primary bases form crystalline sodium salts. The *p*-nitro-derivatives are similar, those derived from primary bases form yellow sodium salts. The following new compounds are described :

Product from toluene- <i>p</i> -sulphonic chloride and	m. p.	<i>p</i> -Nitro- compound. m. p.
Aniline.....	103°	191°
<i>o</i> -Toluidine	108	172
<i>o</i> -Anisidine	127	175
<i>o</i> -Chloroaniline	105	164
<i>p</i> -Xylidine	119	185
<i>o</i> -Amino- <i>p</i> -cresol ethyl ether	112	150
Ethylaniline	87	107
α -Naphthylamine	156	185
Product from benzenesulphonic chloride and		
<i>o</i> -Anisidine	89	181
<i>o</i> -Chloroaniline	127	161

C. H. D.

Behaviour of Aromatic Sulphinic Acids towards Mercuric Salts. WALTER PETERS (*Ber.*, 1905, 38, 2567—2570).—Attempts have been made to prepare isomeric metallic salts of aromatic sulphinic acids ; for example, $R \cdot SO \cdot OM$ and $R \cdot SO_2 \cdot M$ (M = metal), corresponding with Otto's isomeric esters (*Abstr.*, 1880, 810 ; 1885, 1232), but without success.

Mercuric p-toluenesulphinate, $(C_6H_4Me \cdot SO \cdot O)_2Hg$, is obtained when an aqueous solution of mercuric acetate is added to a dilute alcoholic solution of the sulphinic acid at 0°. Although soluble in pyridine and in hot nitric or acetic acid, it has not been obtained in a crystalline form.

When an aqueous alcoholic solution of the sulphinic acid and mercuric chloride in molecular proportions is heated just to boiling, mercury *p*-tolyl chloride (*Abstr.*, 1882, 732) is formed.

Mercury phenyl chloride has been prepared in a similar manner.

J. J. S.

Action of Acetylene Tetrabromide and Aluminium Chloride on Toluene. JAMES LAVAUX (*Compt. rend.*, 1905, 141, 204—206. Compare this vol., i, 43, 125 ; Anschütz and Romig, *Abstr.*, 1885, 768).—The solid product formed by the interaction of acetylene tetrabromide, aluminium chloride, and toluene, consists of a mixture of *A*- and *B*-dimethylantracenes, melting at 240° and 244.5° respectively, with traces of β -methylantracene. The melting point 225°, observed by Anschütz and Romig, is that of a mixture of about equal parts of *A*- and *B*-dimethylantracenes. The yield of dimethylantracenes is more constant, and is increased from 10—20 to 42 per

cent. of the theoretical, and at the same time the formation of resinous products is diminished if the reacting mixture is shaken during the whole course of the reaction. The liquid product contains, in addition to unchanged toluene, benzene, xylene, trimethylbenzene, and other benzene homologues. G. Y.

Triphenylmethyl. XII. MOSES GOMBERG and LEE H. CONE (*Ber.*, 1905, **38**, 2447—2458. Compare *Abstr.*, 1901, i, 77, 319, 638, 690; 1902, i, 534, 600, 754; 1903, i, 81, 244; 1904, i, 658, 988; this vol., i, 426).—Triphenylmethyl forms additive compounds of the type $\text{CRR':O}(\text{CPh}_3)_2$, with the following ketones and ethers: methyl ethyl, diethyl, methyl propyl, methyl butyl, and dipropyl ketones; acetylacetone; methyl hexyl ketone; acetophenone; diethyl, methyl propyl, and ethyl propyl ethers; methylal; phenetole; anisole; benzyl ethyl ether; *o*-tolyl methyl ether. The composition of the additive compounds is determined usually by decomposition at $110\text{--}130^\circ$, of the additive compounds with phenetole and anisole at $110\text{--}130^\circ$ in a vacuum; the additive compounds with the less volatile ketones and ethers are oxidised to triphenylmethyl peroxide. The low percentages of ketones and ethers found for the additive compounds with the ketones and ethers of high boiling point are due probably to superficial decomposition during the necessary washing with light petroleum. The hydrocarbon does not form an additive compound with acetone or isobutaldehyde.

No additive compound of triphenylmethyl and acetonitrile could be obtained. With propionitrile, the compound $\text{CEt:N}(\text{CPh}_3)_2$ is formed in transparent, colourless crystals. With benzonitrile, the hydrocarbon forms an *additive compound*, which crystallises in thin, white needles, is stable in an indifferent atmosphere, and has probably the constitution $(\text{CPh}_3)_2\text{C}_6\text{H}_5\cdot\text{C:N}(\text{CPh}_3)_2$.

On adding warm alcohol to a solution of triphenylmethyl in chloroform and cooling the mixture, a crystalline product is obtained, which, after repeated washing with absolute alcohol and light petroleum and drying in a vacuum, loses 6.7 per cent. at 110° , 72 per cent. of the volatile part consisting of chloroform. On adding ethyl or *iso*-propyl alcohol to the solution of triphenylmethyl in carbon disulphide, crystals are obtained containing 7.8—10.35 per cent. of carbon disulphide and only traces of alcohol. Crystals obtained by the precipitation of triphenylmethyl from its solution in carbon disulphide by adding light petroleum lose 0.14—0.5 per cent. at 110° , the volatile part consisting chiefly of carbon disulphide. The formation of additive compounds by addition of two triphenylmethyl groups to an unsaturated linking or to an atom which can act with a higher valency agrees with the peroxide and iodide formation in pointing to the constitution CPh_3 . If Ullmann and Borsum's compound is benzhydryl-tetraphenylmethane (Tschitschibabin, this vol., i, 125), its formation from Gomberg's triphenylmethyl is not explained by supposing the latter to be hexaphenylethane. Moreover, triphenylmethyl is colourless in the solid state, but forms intensely yellow solutions, a behaviour not in agreement with the properties of saturated hydrocarbons.

The chemical behaviour of triphenylmethane cannot be explained by

Jacobson's formula (this vol., i, 186), which, however, takes into account the dimolecular state of triphenylmethyl. G. Y.

Phenylchrysofluorene. FRITZ ULLMANN and ANNA MOURAWIEW-WINIGRADOFF (*Ber.*, 1905, **38**, 2213—2219).—Diphenyl- α -naphthylcarbinol, $C_{10}H_7 \cdot CPh_2 \cdot OH$ (Acree, *Abstr.*, 1904, i, 360), is easily prepared from phenyl α -naphthyl ketone and magnesium phenyl bromide, and on reduction gives diphenyl- α -naphthylmethane. On heating the carbinol with aniline hydrochloride and glacial acetic acid, with acetic acid containing sulphuric acid or zinc chloride, or with alcoholic zinc chloride, *phenyl chrysofluorene*, $\begin{smallmatrix} C_{10}H_6 \\ | \\ C_6H_4 \end{smallmatrix} > CHPh$, is obtained; it crystallises from glacial acetic acid in long, lustrous needles, melts at 195.5° , and, on oxidation with sodium dichromate in acetic acid solution, gives *o*-benzoylbenzoic acid. *Phenyl chrysofluorenol*, $\begin{smallmatrix} C_{10}H_6 \\ | \\ C_6H_4 \end{smallmatrix} > CPh \cdot OH$, obtained by the action of magnesium phenyl bromide on chrysofluorenone (Graebe, this vol., i, 82), crystallises from benzene or carbon tetrachloride on adding light petroleum in large, lustrous, slightly yellow prisms and melts at 149.5° . On reduction with zinc dust in glacial acetic acid, phenylchrysofluorene is obtained, identical with the substance already described.

Aminodiphenylchrysofluorene, $\begin{smallmatrix} C_{10}H_6 \\ | \\ C_6H_4 \end{smallmatrix} > CPh \cdot C_6H_4 \cdot NH_2$, obtained by heating chrysofluorenol with aniline hydrochloride and glacial acetic acid, separates in small, colourless crystals and melts at 215° .

Diphenyl- β -naphthylcarbinol, $C_{10}H_7 \cdot CPh_2 \cdot OH$, cannot be prepared from methyl β -naphthoate and magnesium phenyl bromide, but is easily obtained by the action of the latter on phenyl β -naphthyl ketone; it crystallises from a mixture of ether and light petroleum in large prisms, melts at 115.5° , and, when heated with glacial acetic acid and concentrated hydrochloric acid, gives *phenyl-phenylene β -naphthylenemethane*, $\begin{smallmatrix} C_{10}H_6^\beta \\ | \\ C_6H_4 \end{smallmatrix} > CHPh$, crystallising from benzene and melting at 137° . W. A. D.

Acetylation in Aqueous Solutions. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and HENRI BARBIER (*Bull. Soc. chim.*, 1905, [iii], **33**, 783—787).—12.3 grams of acetic anhydride dissolve in 120 c.c. of cold water, yielding a solution which readily acetylates amino- and imino-compounds. Thus, aniline or a solution of aniline in dilute acetic acid, when shaken with the anhydride solution, gives an almost theoretical yield of acetanilide. A solution of aniline hydrochloride gives no precipitate when shaken with the anhydride solution, unless sodium acetate is added.

The following acetyl derivatives have been prepared by this method: acetanilide, *o*-acetotoluidide, acetoxylidide, acetomethylanilide, aceto-*p*-phenetidide, acetylphenylhydrazine, diacetyl-*p*-phenylenediamine, *o*-acetylaminophenol, *p*-acetylaminophenol, 2:4-diacetyldiaminophenol, acetylanthranilic acid, acetylphenylglycine. Acetyl-*p*-hydroxyphenyl-

glycine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NaAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which cannot be obtained by boiling hydroxyphenylglycine with acetic anhydride, is readily prepared by dissolving hydroxyphenylglycine in sodium carbonate solution and shaking with the aqueous solution of acetic anhydride. It crystallises from water in colourless prisms melting at 203° and dissolves readily in alcohol or hot water, but only sparingly in ether, chloroform, or benzene. J. J. S.

Crystalline and Liquid Modifications of Formanilide and *p*- and *o*-Formotoluidides. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 439—442).—The interaction of formylglycerol and aniline yields two modifications of formanilide: (1) a crystalline form, melting at 245° , to which the author gives the constitution $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{NH} \\ | \\ \text{H}\cdot\text{C}\cdot\text{O} \end{array}$; (2) a liquid form, $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{N} \\ | \\ \text{H}\cdot\text{C}\cdot\text{OH} \end{array}$. The ordinary form melting at 46° has the structure $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{N} \\ | \\ \text{OH}\cdot\text{C}\cdot\text{H} \end{array}$. The second and third modifications give the compound $\text{NPhNa}\cdot\text{CHO}$ when treated with sodium hydroxide, but the tautomeric form resembles acetanilide in yielding no sodium derivative. Similar modifications of *p*- and *o*-formotoluidides were obtained. T. H. P.

Action of Ethyl Chloroacetate on the Magnesium Halogen Compound of *o*-Toluidine. F. BODROUX (*Compt. rend.*, 1905, 141, 195—196. Compare this vol., i, 427).—Ethyl chloroacetate reacts with the magnesium iodide derivative of *o*-toluidine in ethereal solution to form iodoaceto-*o*-toluidide. If, as sometimes happens, the magnesium halogen compound undergoes spontaneous coagulation, the yield of iodoaceto-*o*-toluidide is very small, the chief product being ethyl iodoacetate.

Iodoaceto-o-toluidide crystallises in long, white needles and melts and decomposes at 142° .

The action of ethyl chloroacetate on the magnesium bromide derivative of *o*-toluidine leads to the formation of chloroaceto-*o*-toluidide in a 50 per cent. yield, along with a compound which melts below 95° and has not been obtained in a state of purity.

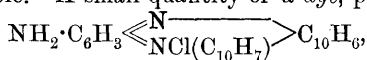
Dichloroaceto-o-toluidide, formed by the action of ethyl dichloroacetate on the magnesium bromide or, along with a small quantity of an iodine compound, on the magnesium iodide derivative of *o*-toluidine, crystallises in long, white needles and melts at 134° . *Trichloroaceto-o-toluidide*, formed in the same manner from ethyl trichloroacetate, crystallises in long, white needles and melts at 95° . G. Y.

Condensation Products of Primary Aromatic Amines with Formaldehyde. FARBERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158543).—It was shown by Pulvermacher (Abstr., 1892, 1450) that the nitroanilines react with formaldehyde in alcoholic solution to form methylene derivatives. It is found that formaldehyde also reacts with salts of the aromatic nitro-amines in aqueous solution. Thus, 4-nitro-2-aminotoluene hydrochloride and formaldehyde yield

the compound $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_2$, which crystallises from alcohol and acetic acid in glistening, yellow needles and melts at 230° ; it is insoluble in cold dilute acids. The corresponding compound from *o*-nitro-*p*-toluidine forms orange needles and melts at 254° .

C. H. D.

1:1'-Dichloro-2:2'-dinaphthylamine. WLADIMIR G. SCHAPO-SCHNIKOFF and F. GOLEFF (*Zeit. Farb. Text. Ind.*, 1905, 4, 281—283).—On adding $\beta\beta$ -dinaphthylamine dissolved in glacial acetic acid to quinonedichlorodi-imine dissolved in the same solvent, keeping the temperature below 45° , 1:1'-dichloro-2:2'-dinaphthylamine, $\text{NH}(\text{C}_{10}\text{H}_6\text{Cl})_2$, is obtained; it crystallises from glacial acetic acid or benzene in needles, melts at 145° , and on heating with lime gives rise to naphthacarbazole. A small quantity of a dye, probably



is also formed; it gives a red hydrochloride crystallising in needles, is easily acetylated and diazotised.

From the foregoing experiments, dichloroquinonedi-imine appears capable of acting as a chlorinating agent.

W. A. D.

Action of Sulphur on the Organo-magnesium Derivatives of *p*-Bromo-anisole and -phenetole. F. TABOURY (*Bull. Soc. chim.*, 1905, [iii], 33, 836—839. Compare Abstr., 1903, i, 748; 1904, i, 493).—*p*-Methoxy- and *p*-ethoxy-thiophenols (Abstr., 1892, 1089) are formed by the action of sulphur, followed by acidified water, on the magnesium derivatives of *p*-bromo-anisole and -phenetole. The corresponding disulphides are not formed as by-products, but may be obtained by the action of hydrogen peroxide on the thiophenols.

Acyl chlorides react with these magnesium compounds yielding aryl thiocarboxylates. *p*-Methoxyphenyl thioacetate, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{COMe}$, is an oil distilling at 163 — 166° under 12 mm. pressure. The corresponding thiobenzoate crystallises from alcohol in slender needles melting at 99 — 100° . *p*-Ethoxyphenyl thioacetate melts at 41 — 42° and the corresponding thiobenzoate at 106° .

Alkyl haloids react with the magnesium compounds yielding alkyl sulphides. Benzyl *p*-methoxyphenyl sulphide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\text{Ph}$, melts at 45 — 46° , and benzyl *p*-ethoxyphenyl sulphide at 43 — 44° .

J. J. S.

Phenylation of Phenols. FRITZ ULLMANN, PAUL SPONAGEL [and, in part, STEIN] (*Ber.*, 1905, 38, 2211—2212).—When potassium phenoxide is heated with bromobenzene for twelve hours at 180 — 210° , the yield of diphenyl ether obtained is only 0.9 per cent. of the theoretical; on adding a small quantity of copper, however, and heating for two hours at 210 — 230° , 87 per cent. of the theoretical quantity of diphenyl ether is obtained. *o*-Methoxydiphenyl ether, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, may be prepared similarly from guaiacol, and phenoxybenzoic acid from salicylic acid. Bromobenzene may also in this method of preparation be replaced by its homologues. *m*-Nitrodiphenyl ether, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared from *m*-bromonitrobenzene, is

a yellow oil which boils at 198—200° under 14 mm. pressure. From phenol and *p*-dibromobenzene, *quinol diphenyl ether*, $C_{18}H_{14}O_2$, is obtained; it melts at 77° and boils at 371—372° under 720 mm. pressure. *Phloroglucinol triphenyl ether*, obtained from *s*-tribromobenzene, melts at 110°. W. A. D.

Condensation of Chloral with Aromatic Hydrocarbons under the Influence of Aluminium Chloride. ADOLPHE DINES-MANN (*Compt. rend.*, 1905, 141, 201—203. Compare Combes, *Abstr.*, 1884, 837; Fritsch, *Abstr.*, 1897, i, 568).—The action of chloral on benzene, toluene, *p*-xylene, and anisole in presence of aluminium chloride leads to the formation of the corresponding phenyltrichloromethylcarbinols.

Phenyltrichloromethylcarbinol, formed by this reaction, melts at 37°, boils at 145° (corr.) under 15 mm. pressure, and is identical with Jocitsch's compound, prepared by the action of chloral on magnesium phenyl bromide (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 96). It reduces ammoniacal silver nitrate and Fehling's solution, yields with benzoyl chloride the *benzoyl* derivative, $OBz \cdot CHPh \cdot CCl_3$, which crystallises in needles and melts at 97—98°, and is reduced by zinc dust and acetic acid to dichlorostyrene (Jocitsch and Faworsky, *Abstr.*, 1899, i, 786). With fuming nitric acid, dichlorostyrene yields a *nitro*-derivative which melts at 93° and is reduced by zinc and acetic acid to an *amine* melting at 99—100° and an *azo*-compound crystallising in red lamellæ and melting at 146—147°.

p-Tolyltrichloromethylcarbinol, prepared by condensation of chloral with toluene, melts at 63—64°, boils at 154—156° under 13·5 mm. pressure, and is identical with Jocitsch's compound formed from chloral and magnesium *p*-tolyl bromide (*loc. cit.*). The *acetate* melts at 107—108°; the *benzoate* melts at 100—101°. On oxidation with chromic acid, the carbinol yields a mixture of the corresponding ketone with unchanged carbinol, which, when treated with alkali hydroxides, is decomposed with formation of chloroform and *p*-toluic acid.

p-Xyliltrichloromethylcarbinol, $C_8H_9 \cdot CH(OH) \cdot CCl_3$, melts at 61—61·5°. The *acetate* melts at 85—87°; the *benzoate* melts at 112·5—113·5°.

p-Methoxyphenyltrichloromethylcarbinol, $OMe \cdot C_6H_4 \cdot CH(OH) \cdot CCl_3$, melts at 55—56°, boils at 184—186° under 16 mm. pressure, and forms an *acetate* melting at 79—81°. When oxidised with chromic acid and treated with potassium hydroxide, the carbinol yields chloroform and anisic acid. G. Y.

[*p*-Methoxyphenylethylcarbinol.] AUGUST KLAGES (*Ber.*, 1905, 38, 2219—2222).—Polemical (compare *Abstr.*, 1904, i, 487, and this vol., i, 344; Hell, this vol., 436). W. A. D.

Preparation of ω -Cyanomethylanthranilic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158346).—Formaldehyde combines with anthranilic acid in aqueous suspension or ethereal solution to form a *compound*, separating in yellowish-white crystals, melting and decomposing at about 145—150°, insoluble in cold dilute alkalis or

acids, readily soluble in acetone. The product, which shows strong triboluminescence, is not a Schiff's base. Potassium cyanide or hydrocyanic acid reacts with it, yielding ω -cyanomethylantranilic acid.

C. H. D.

Hydroxymethyl Derivatives of Amides. ALFRED EINHORN (D.R.-P. 158088).—The hydroxymethyl derivatives of amides, $\text{RCO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}$ (this vol., i, 344), may be prepared by the action of formaldehyde on amides in the presence of acid condensing agents instead of alkalis, if precautions are taken to prevent the reaction from extending further to the formation of methylenediamine derivatives. Thus, when benzamide and formaldehyde are warmed with dilute sulphuric acid at 25° until completely dissolved, and immediately precipitated by sodium acetate, hydroxymethylbenzamide is obtained. The preparation of hydroxymethylsalicylamide is also described.

C. H. D.

Claisen's Cinnamic Acid Synthesis. ARTHUR MICHAEL (*Ber.*, 1905, 38, 2523—2524).—A reply to Stoermer and Kippe (this vol., i, 526).

A. McK.

Formation of Liebermann's *iso*Cinnamic Acid by the Resolution of *allo*Cinnamic Acid with Brucine. EMIL ERLENMEYER, jun. (*Ber.*, 1905, 38, 2562—2565. Compare this vol., i, 193).—A very small amount of *allocinnamic* acid is formed when cinnamaldehyde is incompletely oxidised. When a mixture of brucine and *allocinnamic* acid is crystallised from absolute alcohol, a crystalline *brucine* salt melting at 151° is obtained. The yield is about 50 per cent., and the salt, when decomposed with dilute sulphuric acid, yields Liebermann's *isocinnamic* acid (*Abstr.*, 1890, 494, 620), which crystallises from light petroleum in large, monoclinic crystals

$$[a : b : c = 0.5555 : 1 : 0.4053 ; \beta = 70^\circ 8']$$

melting at 58 — 59° . Complete crystallographic data are given. The mother liquor from the crystalline salt melting at 151° yields a syrup which solidifies and then melts at 110 — 120° ; this product is under investigation.

Liebermann's *isocinnamic* acid appears to be a component of *allocinnamic* acid. Cinnamic acid itself yields but one brucine salt. Erlenmeyer's *isocinnamic* acid may be obtained when an aqueous sulphuric acid solution of the *allo*-acid is kept for some time.

J. J. S.

***p*-Chloroacetylphenoxyacetic Acid and Ethyl *p*-Chloroacetylphenylacetate.** FRANZ KUNCKELL (*Ber.*, 1905, 38, 2609—2611).—Acyl groups, for example, chloroacetyl, can be readily introduced into phenylacetic and phenoxyacetic acids and their esters by means of the Friedel-Crafts synthesis, using carbon disulphide as diluent.

p-Chloroacetylphenoxyacetic acid, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, crystallises from hot water in glistening plates, melts at 146 — 147° , and is readily soluble in ether, alcohol, or chloroform. The sodium, silver, and cupric salts have been prepared.

Ethyl p-chloroacetylphenylacetate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, crystallises from a mixture of ether and light petroleum in colourless needles, melts at $56\text{--}58^\circ$, and dissolves readily in alcohol or ether.

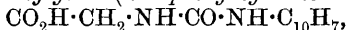
J. J. S.

Derivatives of Indoxylic Acid. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 158089).—Phenylglycinecarboxylic esters are converted into indoxylic esters by heating with sodium ethoxide (Vorländer and Schilling, Abstr., 1898, i, 682). It is found that esters or amides of the general formula $\text{R}'\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NR}'''\cdot\text{CH}_2\cdot\text{COR}''$ (where R' and R'' are alkyloxy-, amino-, or alkylamino-groups, and R''' is hydrogen or acyl) are readily converted into indoxylic esters when heated with sodamide or its substituted derivatives in presence of an indifferent liquid at temperatures below 130° . If fused, indoxyl is formed (Abstr., 1903, i, 632). Thus an almost theoretical yield of ethyl indoxylate is obtained on heating ethyl phenylglycine-*o*-carboxylate with sodioacetanilide and xylene at $125\text{--}130^\circ$.

*Ethyl p-bromophenylglycine-*o*-carboxylate* melts at 97° and when heated with sodioacetanilide and xylene yields *ethyl bromoindoxylate*, separating from dilute alcohol in green crystals and melting at $152\text{--}154^\circ$. Other preparations are described in detail. C. H. D.

Isolation of Amino-acids. CARL NEUBERG and ALBERT MANASSE (*Ber.*, 1905, **38**, 2359—2366. Compare E. Fischer and Bergell, Abstr., 1903, i, 24; Siegfried, this vol., i, 59; Hinsberg, Abstr., 1901, i, 128).—Amino-acids yield well-crystallised additive products with α -naphthylcarbimide, and the yield is quantitative when the carbimide is shaken for a few minutes with an alkaline solution of the amino-acid without artificial cooling, and then left for $\frac{1}{2}\text{--}\frac{3}{4}$ hour. The solution is filtered to remove dinaphthylcarbamide and the filtrate acidified, when the naphthylhydantoic acid is precipitated. Good results have been obtained with α - and β -amino-acids, amino-aldehydes, aminohydroxy-acids, diamino-acids, and peptides. Amino-acids may be estimated in urine in a similar manner after the removal of albumin. Hippuric acid does not react with the naphthylcarbimide.

α -Naphthylcarbimideglycine (α -naphthylhydantoic acid),



crystallises from alcohol in colourless needles and melts at $190\cdot5\text{--}191\cdot5^\circ$. It dissolves in alkalis and yields an insoluble *barium* salt.

α -Naphthylcarbimide- γ -alanine, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, melts at 198° , and its *barium* salt is moderately soluble in water. The following have also been prepared :

Acid.	M. p. of α -naphthylcarbimide.
<i>r</i> - α -Amino- <i>n</i> -butyric acid	194—195°.
Leucine	163·5
<i>l</i> -Tyrosine	205—206
Glycylglycine	217
Glutamic acid ..	236—237
Cystine.....	Alkali salts sparingly soluble.

Diphenylcarbamide chloride reacts with amino-acids in the presence of alkali, yielding substituted carbamides. The reaction proceeds readily on warming. Diphenylhydantoic acid (*glycinediphenylcarbamide*), $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NPh}_2$, crystallises in glistening, hexagonal plates and melts at $144\cdot5^\circ$. J. J. S.

Use of Phenyl Ether in the Friedel-Crafts Reaction. HERMANN KIPPER (*Ber.*, 1905, 38, 2490—2493).—Phenyl ether reacts with acid chlorides or acid anhydrides in molecular proportions in the presence of aluminium chloride.

p-Phenoxyacetophenone, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$, prepared from phenyl ether, acetyl chloride, and aluminium chloride, boils at $318\text{--}325^\circ$ and melts at 45° (corr.). It forms an intensely yellow solution with sulphuric acid.

β -*p*-Phenoxybenzoylpropionic acid, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_2\text{H}_4\cdot\text{CO}_2\text{H}$, prepared from phenyl ether, succinic anhydride, and aluminium chloride, separates from aqueous alcohol in glistening leaflets and melts at 117° (corr.). Its solution in sulphuric acid is intensely yellow.

p-Phenoxybenzophenone, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$, prepared from phenyl ether, benzoyl chloride, and aluminium chloride, separates from aqueous alcohol in glistening needles and melts at 71° (corr.). Its solution in sulphuric acid is yellow.

p-Phenoxybenzoylbenzoic acid, $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared from phenyl ether, phthalic anhydride, and aluminium chloride, separates from aqueous alcohol in glistening needles and melts at $163\cdot5^\circ$ (corr.). Its solution in sulphuric acid is red. A. McK.

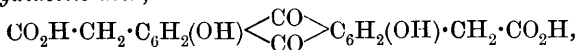
Hydroxyanthraquinoneglycollic [Anthraquinoneoxyacetic] Acids and their Esters. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158277).—The metallic derivatives of hydroxyanthraquinones react with alkyl chloroacetates or bromoacetates to form anthraquinoneoxyacetic esters corresponding with phenoxyacetic esters. The crystalline esters are readily saponified by alkali hydroxides, and the acids may be precipitated from solutions of the salts thus obtained.

Ethyl anthraquinone-2-oxyacetate, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\rangle\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, prepared by boiling sodium 2-hydroxyanthraquinone with ethyl chloroacetate in a reflux apparatus, forms yellowish-white needles, melts at 135° , and distils without decomposition; it dissolves readily in benzene or acetic acid, sparingly in alcohol or ether. Sulphuric acid dissolves it to an orange solution. *Sodium anthraquinone-2-oxyacetate* is crystalline and dissolves in water to a pale yellow solution. The acid separates from glacial acetic acid as a yellowish-white powder, melts at $234\text{--}235^\circ$, and dissolves less readily in organic solvents than the ethyl ester.

Ethyl anthraquinone-1-oxyacetate forms yellow needles and melts at $174\text{--}175^\circ$. The corresponding ester from alizarin crystallises from benzene in orange leaflets and melts at $165\text{--}166^\circ$. It yields a red, sparingly soluble sodium salt, which is hydrolysed on boiling to the

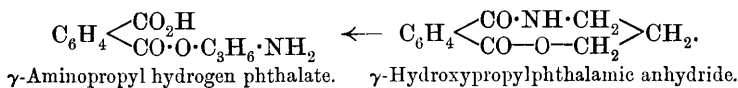
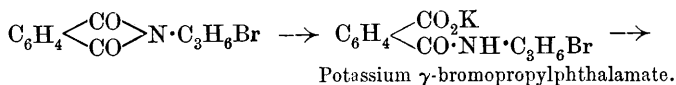
readily soluble *sodium* salt of the glycollic acid. The *acid* separates from acetic acid in orange crystals and melts at 267—268°.

The *diglycollic* ester from the tetrasodium derivative of anthrachryson and ethyl bromoacetate forms yellow needles and melts at 227—229°, and on hydrolysis yields 4:8-*dihydroxyanthraquinone-2:6-dioxydiacetic acid*,



which melts above 290° and dissolves very sparingly in organic solvents. C. H. D.

Derivatives of β -Aminoethyl- and of α -Aminopropyl-alcohol. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 2389—2404. Compare Abstr., 1890, 472).—The reaction between γ -bromopropylphthalimide and alkalis does not consist of the mere replacement of bromine by hydroxyl, but in the following series of transformations:



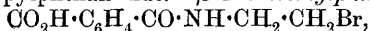
γ -Aminopropyl hydrogen phthalate is formed when the bromo-compound is heated with alcoholic potassium hydroxide for 15 minutes. It crystallises with $1\text{H}_2\text{O}$ in rhombic plates, and when quickly heated melts at 168—169°, but water is eliminated at the same time, and γ -hydroxypropylphthalimide, melting at 75°, is formed. It dissolves in both acids and alkalis; the *hydrochloride*, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}\cdot\text{HCl}$, begins to sinter at 160° and melts to a clear liquid at 163·5°. The *platinichloride* crystallises in flat needles, and when slowly heated melts at 204—205°.

The *methyl* ester, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_3\text{H}_6\cdot\text{NH}_2$, is an oil which yields a strongly alkaline aqueous solution and a *hydrochloride* melting at 124—125°.

When bromopropylphthalimide is shaken with cold 4*N* aqueous potassium hydroxide and then acidified, γ -bromopropylphthalamic acid is obtained. It crystallises from ethyl acetate in flat needles and melts at 107—108°. When warmed with hydrobromic acid of different concentrations, it is either transformed into bromopropylphthalamide or hydrolysed to bromopropylamine hydrobromide and phthalic acid. With alcoholic potash, it is ultimately converted into γ -aminopropyl hydrogen phthalate, but yields as an intermediate product *anhydro- γ -hydroxypropylphthalamic acid*, which is readily purified by conversion into the sparingly soluble nitrosoamine (see following abstract). The *hydrochloride*, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}\cdot\text{HCl}$, of the anhydro-base melts at 137°, dissolves extremely readily in water and moderately in alcohol. It is readily hydrolysed to the hydrochloride of γ -aminopropyl hydrogen phthalate when its aqueous solution is warmed, but in the presence of a relatively large amount of alkali the base is comparatively stable. The *aureichloride*, $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}\cdot\text{HAuCl}_4$,

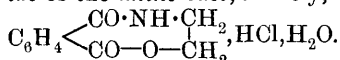
crystallises in golden-yellow, flat needles and melts at 198—199°, the *platinichloride* melts and decomposes at 193°, and the *picrate* melts at 182°. The *base* crystallises in glistening, felted needles, melts at 136°, and is readily soluble in water but insoluble in ether. It readily combines with water forming the *hydrate*, $C_{11}H_{11}O_3N \cdot 3H_2O$, which crystallises in glistening plates or prisms melting at 72—73°. When distilled, the hydrochloride is converted into γ -chloropropylphthalimide, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot C_3H_6Cl$, which crystallises from light petroleum in prisms melting at 67—68°.

The transformation of β -bromoethylphthalimide into the corresponding β -hydroxy-compound proceeds in a manner similar to that described for the γ -bromopropylphthalimide. β -Bromoethylphthalamic acid,



crystallises from ethyl acetate in compact needles melting at 125.5°.

The compound previously described as the hydrochloride of hydroxyethylphthalamic acid (Abstr., 1888, 440) is shown to be the *hydrated hydrochloride* of the *imino-base*, namely,



It begins to sinter at 87° and melts at 91—92°. The *base* crystallises from alcohol, melts at 139°, and is readily soluble in acids and alkalis. The *aurichloride* softens at 155° and melts at 169—171°; the *platinichloride* crystallises in compact, golden-yellow prisms, turns yellow at 187°, and then darkens and decomposes. When distilled under reduced pressure the imino-base is converted into β -hydroxyethylphthalimide and, when evaporated with hydrobromic acid, into β -bromoethylphthalimide. With aqueous potassium hydroxide, it

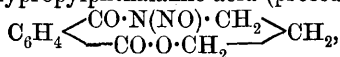
yields a *potassium salt*, $C_6H_4 \begin{smallmatrix} \diagup CO \cdot NK \cdot CH_2 \\ \diagdown CO - O - CH_2 \end{smallmatrix}$, which is sparingly soluble

in excess of the alkali. When the potassium salt is heated with benzyl chloride and then hydrolysed with fuming hydrobromic acid, β -bromoethylbenzylamine is formed. When heated for a short time with water, the base is converted into β -aminoethyl hydrogen phthalate, $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, which melts and decomposes at 149—150°. The *hydrochloride*, $C_{10}H_{11}O_4N \cdot HCl$, melts and decomposes at 189° and the *platinichloride* at about 220°. The *hydrochloride* of the *methyl ester*, $CO_2Me \cdot C_6H_4 \cdot CO_2 \cdot C_2H_4 \cdot NH_2 \cdot HCl$, crystallises in six-sided plates and melts at 130—131°; the ester itself is an oil.

J. J. S.

Nitroso-derivatives of Oxygenated Imino-compounds.

SIEGMUND GABRIEL (*Ber.*, 1905, 38, 2405—2413).—The *nitrosoamine* of anhydro- γ -hydroxypropylphthalamic acid (preceding abstract),



separates from boiling alcohol in crystals resembling gypsum; it melts and decomposes at 123°, is soluble in most organic solvents, and is decomposed when heated with hydrochloric acid or boiled for some time with alcohol. When warmed with a dilute potassium hydroxide solution, it yields nitrogen, phthalic acid, and trimethyleneglycol.

The *nitrosoamine*, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{NO}) \\ \text{CO} \cdot \text{O} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, obtained from β -bromoethylphthalimide, crystallises in pale yellow plates and melts and decomposes at 137° . When warmed with dilute alkali, it yields phthalic acid, acetylene, and nitrogen.

The *nitrosoamine*, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{NO}) \\ \text{CO} \cdot \text{O} \cdot \text{CHMe} \end{smallmatrix} > \text{CH}_2$, obtained from β -bromopropylphthalimide, crystallises in four-sided prisms and melts at 147 – 148° . When warmed with dilute sodium hydroxide, it yields phthalic acid, allylene, and nitrogen.

The *nitrosoamine*, $\text{CO} \begin{smallmatrix} \text{N}(\text{NO}) \\ \text{O} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, obtained from hydroxyethylcarbamic anhydride (Gabriel and Eschenbach, Abstr., 1898, i, 62), crystallises from a mixture of ethyl acetate and light petroleum in long, silky needles melting at 53° , and readily soluble in most organic solvents. It is somewhat unstable and readily decomposes on exposure to the air, leaving a soft, resinous substance; when dissolved in dilute sodium hydroxide, it yields nitrogen and acetylene, but the amount of acetylene does not correspond with the equation $C_3H_4O_3N_2 = CO_2 + H_2O + N_2 + C_2H_2$.

Benzamidoethyl benzoate, $CO_2Ph \cdot CH_2 \cdot CH_2 \cdot NH \cdot COPh$, obtained by benzoylating aminoethyl benzoate (Gabriel and Heymann, Abstr., 1890, 1267), crystallises from ether in flat needles melting at 88 – 89° . A nitrosoamine could not be prepared in benzene solution, probably owing to the absence of basic properties.

Pyrrolidone yields an oily *nitrosoamine*, $\begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{N} \cdot \text{NO}$, which reacts with dilute sodium hydroxide, yielding nitrogen and γ -butyrolactone.

Ethyl bromoethyloxamate, $CO_2Et \cdot CO \cdot NH \cdot C_2H_4Br$, obtained from bromoethylamine hydrobromide, potassium hydroxide, and ethyl oxalate at 0° , crystallises from light petroleum in long, glistening needles and melts at 61° . It has not been found possible to convert it into a cyclic imine by the elimination of ethyl bromide. J. J. S.

Reduction of Derivatives of Dinitrodiphenylmethane. H. DUVAL (*Compt. rend.*, 1905, 141, 198–201).—4:4'-Dicyanodiphenylmethane, formed from 4:4'-diaminodiphenylmethane, melts on Maquenne's block at 169° , and the corresponding dicarboxylic acid at 323° (m. p. 165° and 290° respectively, Schöpf, Abstr., 1894, i, 600). Nitration of the dicarboxylic acid in a mixture of nitric and sulphuric acids leads to the formation of *dinitrodiphenylmethane-4:4'-dicarboxylic acid*, which melts at 278° , is soluble in acetone, alcohol, boiling acetic acid, or nitrobenzene, and on treatment with hydrogen chloride in alcoholic solution yields *ethyl dinitrodiphenylmethane-4:4'-dicarboxylate*; this crystallises from alcohol and melts at 117° . *Ethyl diaminodiphenylmethane-4:4'-carboxylate*, formed by reduction of the dinitro-ester with zinc dust and ammonium chloride in boiling alcoholic solution, crystallises in needles, melts at 148° , is soluble in benzene, ether, acetone, or hot alcohol, and on hydrolysis with alcoholic potassium hydroxide yields *diaminodiphenylmethane-4:4'-dicarboxylic acid*, which

crystallises from alcohol, melts at 329° , and dissolves in aqueous alkali hydroxides or acids.

The reduction of 2:2'-dinitro-4:4'-diaminodiphenylmethane (Schnitzspahn, Abstr., 1902, i, 436) by means of zinc dust and ammonium chloride in alcoholic solution leads to the formation of 4:4'-diamino-2:2'-azoxydiphenylmethane, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{N}_2\text{O} \\ \text{CH}_2 \end{smallmatrix} > \text{C}_6\text{H}_3 \cdot \text{NH}_2$, which crystallises in yellow needles, melts at 272° , and when boiled with zinc dust in alcoholic potassium hydroxide solution yields 4:4'-diamino-2:2'-azodiphenylmethane, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{N}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{C}_6\text{H}_3 \cdot \text{NH}_2$, melting at 233° .
G. Y.

Gradual Dissociation of Mellitic Acid. ANTONIO QUARTAROLI (*Gazzetta*, 1905, 35, i, 470—477).—Towards indicators, mellitic acid behaves as either a tervalent or a sexavalent acid, which would indicate a considerable difference between K_3 and K_4 . The magnitudes of the six dissociation constants, K_1 , K_2 , K_3 , &c., of the acid and its uni-, bi-, ter-, &c., metallic salts have been determined by the inversion of sucrose method. Taking K_1 as 100, $K_2 = 40.463$, $K_3 = 14.315$, $K_4 = 2.205$, $K_5 = 1.490$, and $K_6 = 1.039$. These numbers give the following ratios: $K_1/K_2 = 2.47$; $K_2/K_3 = 2.82$; $K_3/K_4 = 6.49$; $K_4/K_5 = 1.47$, $K_5/K_6 = 1.43$, which constitute an exception to the general rule that the difference between two consecutive constants is greater the higher the value of the first of them; with K_4 , K_5 , and K_6 the behaviour conforms to this law.

These irregularities are probably due to the fact that successive saturation of the carboxyl groups by means of alkali takes place not in the order 1, 2, 3, &c., but in the order 1, 3, 5, 2, 4, 6. T. H. P.

Hydrazine Derivatives of o-Aminobenzaldehyde. CESARE RONCAGLIOLO (*Gazzetta*, 1905, 35, i, 510—514).—By treating o-aminobenzaldehyde with monoacylhydrazines, the author has attempted, without success, to obtain compounds containing a seven-atom chain in addition to the benzene nucleus of the aldehyde.

o-Aminobenzylideneacetylhydrazide, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NHAc}$, prepared by the interaction of acetylhydrazine and o-aminobenzaldehyde in molecular proportions, separates from water in small crystals melting at 170° and is readily soluble in alcohol or acetone.

Acetylaminobenzylideneacetylhydrazide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NHAc}$, obtained by the action of acetic anhydride on the preceding compound, is deposited from aqueous solution in transparent, colourless crystals melting at 195 — 196° and is readily soluble in alcohol.

o-Aminobenzaldazine, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} : \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, prepared by the action of a hydrazine salt on an aqueous alcoholic solution of o-aminobenzaldehyde, crystallises from alcohol in small, yellow needles melting at 243° . The diacetyl derivative,

$\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} : \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, crystallises from alcohol in yellow needles melting at 285 — 288° .

T. H. P.

Conversion of Cinnamaldehyde into Cinnamyl Alcohol. PHILIPPE BARBIER and GEORGES LESER (*Bull. Soc. chim.*, 1905, [iii], 33, 858—859).—Cinnamaldehyde itself cannot be reduced in acid, alkaline, or neutral solution, as it immediately polymerises, but its diacetyl derivative, when reduced with iron filings and acetic acid (80 per cent.), yields a product distilling at 120—160° under 14 mm. pressure. When this is hydrolysed with alcoholic sodium hydroxide, pure cinnamyl alcohol is obtained; it melts at 32° and boils at 142—145° under 14 mm. pressure. J. J. S.

Preparation of Cuminoin and Cuminil. HEINRICH BILTZ and CARL STELLBAUM (*Annalen*, 1905, 339, 294—296).—In order to prepare cuminoin, the commercial cuminaldehyde is purified by means of the sodium hydrogen sulphite compound, and then condensed by boiling with an aqueous alcoholic solution of potassium cyanide. The cuminoin is oxidised to cuminil with chromic acid. K. J. P. O.

cycloGeraniolideneacetone. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158075).—*cycloGeraniolenealdehyde* (Abstr., 1903, i, 764) condenses with acetone in the presence of sodium ethoxide, alkali hydroxides, barium hydroxide or borax, with or without the addition of water or alcohol, to form *cyclogeraniolideneacetone*, $\text{CMe}_2 \left\langle \begin{array}{c} \text{CH}=\text{CH} \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \right\rangle \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{COMe}$, a colourless, viscid oil, which boils at 130—135° under 14 mm. pressure and has an odour of roses and violets. C. H. D.

Dinitrodiaminoanthraquinonedioxamic Acids. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158076).—1:5- and 1:8-Diaminoanthraquinones react with oxalic acid at 100—150°, or at lower temperatures if the water is removed as formed, yielding dioxamic acids, $\text{OH} \cdot \text{C}_2\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3 \left\langle \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \right\rangle \text{C}_6\text{H}_3 \cdot \text{NH} \cdot \text{C}_2\text{O}_2 \cdot \text{OH}$, which are almost insoluble in water, but form soluble, yellow alkali salts. Mono-oxamic acids, yielding red salts, are formed at lower temperatures.

Nitric and sulphuric acids convert the dioxamic acids more readily than other acyl derivatives of anthraquinone into dinitro-derivatives. 4:8-Dinitroanthraquinone-1:5-dioxamic acid is orange, and yields 4:8-dinitro-1:5-diaminoanthraquinone on hydrolysis with alkalis.

Sodium sulphide dissolves the dioxamic acids to green solutions, becoming blue when warmed, and depositing bronze crystals of *sodium tetra-aminoanthraquinonedioxamates* on cooling. C. H. D.

1-Hydroxyanthraquinone-5-sulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158413).—Anthraquinone and its sulphonic acids are only oxidised by sulphuric acid to polyhydroxyanthraquinones when highly fuming acid is employed at a low temperature. Acid containing less than 40 per cent. of anhydride at temperatures above 100° only yields sulpho-derivatives. It is found, however, that sulphuric acid with 25—30 per cent. anhydride oxidises anthraquinone-1-sulphonic acid completely at 150° to 1-hydroxyanthra-

quinone-5-sulphonic acid, yielding a yellow, crystalline sodium salt. Heating with milk of lime under pressure converts it into anthrarufin.

C. H. D.

[A New Aminodihydroxyanthraquinonesulphonic Acid.]

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158150).—The purpurin-sulphonic acid previously described (this vol., i, 146) reacts with ammonia rapidly at 120°, more slowly under atmospheric pressure, to form a new *aminohydroxyanthraquinonesulphonic acid*. The reaction is complete when a sample dissolved in sulphuric acid gives a strong yellow fluorescence with boric acid. The new acid dissolves in water to a reddish-violet solution, becoming violet with sodium carbonate, and in hot aniline to a red solution.

C. H. D.

Preparation of *o*-Dimethoxyanthraquinones. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158278).—Nitro-methoxyanthraquinones, in which the nitro- and methoxy-groups are attached to neighbouring carbon atoms, are converted by sodium hydroxide in methyl-alcoholic solution into dimethoxy-derivatives. Other isomerides, such as 4-nitro-1-methoxyanthraquinone, yield only a mixture of nitrohydroxy- and aminomethoxy-anthraquinone.

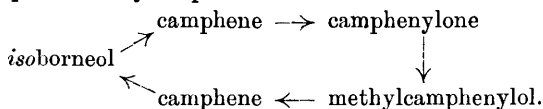
Alizarin dimethyl ether, from 1-nitro-2-methoxyanthraquinone, crystallises from alcohol in yellow needles and melts at 210°. It is not possible to prepare it by direct methylation of alizarin (Graebe and Aders, Abstr., 1902, i, 42). Heating with sulphuric acid converts it into the monomethyl ether.

Anthragallol trimethyl ether, from 1:3-dinitro-2-methoxyanthraquinone, crystallises from alcohol in light brown needles and melts at 160°.

C. H. D.

Methylcamphenylol. ST. MOYCHO and FR. ZIENKOWSKI (*Ber.*, 1905, **38**, 2461—2464. Compare Wagner, Moycho, and Zienkowski, Abstr., 1904, i, 438; Bouveault and Blanc, this vol., i, 222).—The oxidation product, formed by the action of chromic acid in concentrated aqueous solution on methylcamphenylol dissolved in glacial acetic acid, yields a mixture of camphor semicarbazone and a semicarbazone which melts at 215—216° and yields a ketone or mixture of ketones melting at 113—115°.

The camphene formed by dehydration of methylcamphenylol by means of 30 per cent. sulphuric acid boils at 157—158°, and on oxidation with potassium permanganate yields camphenylone, camphenylic acid, and a small proportion of camphenecamphoric acid; with glacial acetic acid and sulphuric acid, it yields *isobornyl acetate*, which completes the cyclic process:



G. Y.

Cyclene Bromide (Solid Pinene Bromide). J. O. GODLEWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 424—438. Compare Abstr., 1899, i, 618 and 920).—The action, at the ordinary temperature, of

silver acetate on solid pinene bromide in acetic acid solution and in absence of light yields sobrerol and the corresponding acetic ester. If the mixture is kept for a long time and is then gradually heated to 100°, it yields pinol, the acetic esters of carveol and sobrerol, and sobrerol itself. The author considers that only sobrerol and its acetic ester are formed directly from the pinene bromide, the other compounds arising from these initial products when the conditions happen to be favourable to such changes. T. H. P.

Reactions of Guaiacum Resin. PAUL PETIT and MAYER (*Compt. rend.*, 1905, 141, 193—195).—In an atmosphere of hydrogen, tincture of guaiacum gives a blue coloration with solutions of ferric or manganic salts containing 0.02 milligram of metal per 100 c.c.; the ferric chloride is gradually reduced to ferrous chloride as shown by the disappearance of the blue colour, the formation of a blue coloration with potassium ferricyanide, and the reappearance of the original blue on addition of hydrogen peroxide. With silver nitrate or carbonate, guaiacum gives a blue coloration, with formation of silver oxide and metallic silver and quantitative liberation of the acid.

Guaiacum gives no blue coloration with ferrous chloride in an atmosphere of hydrogen, but does so immediately on admission of the least trace of air, similarly manganous acetate or lactate, but not the chloride, gives the coloration in contact with air.

In an atmosphere of hydrogen, guaiacum tincture dissolves (a) ferrous oxide to form a colourless solution which becomes blue on exposure to the air, or on addition of hydrogen peroxide; (b) manganous oxide to a colourless solution which becomes blue on contact with air only in presence of traces of acetic or lactic acid; and (c) manganic oxide to a green solution becoming blue on contact with air in presence of traces of an acid, or on addition of hydrogen peroxide.

With ferric oxide, guaiacum forms a compound which is insoluble in water, but soluble in alcohol. The blue colouring matters formed by guaiacum with ferric, manganic, or silver salts dissolve in chloroform or alcohol, or less readily in benzene, to solutions which rapidly decolorise.

In presence of albumin, the sensitiveness of the guaiacum reaction is greatly diminished; this effect is partially neutralised by the presence of an excess of acid. G. Y.

Gentiopicroin. GEORGES TANRET (*Compt. rend.*, 1905, 141, 207—209. Compare Bourquelot and Hérissé, *Abstr.*, 1900, i, 511).—The alcoholic extract of fresh gentian is diluted to 17 per cent. with water, extracted with hot ethyl acetate, and the syrup obtained on evaporation of the extract dried and recrystallised from boiling absolute alcohol. Owing to the presence of about 1 per cent. of gentiin the product gives a coloration with ferric chloride, and must be further purified by recrystallisation from hot ethyl acetate containing 2 per cent. of water, the gentiin accumulating in the mother liquors, which are evaporated finally to dryness, the residue being recrystallised from water and again treated with ethyl acetate. A yield of 70—140 grams of gentiopicroin is obtained in this manner from 1 kilogram of dried alcoholic extract.

Gentiopicroin $C_{16}H_{20}O_9 \cdot \frac{1}{2}H_2O$, forms orthorhombic crystals, melts at 122° ($2C_{20}H_{30}O_{12} \cdot \frac{1}{2}H_2O$, m. p. $120-125^\circ$; Kromayer, *Arch. Pharm.*, 110, 25), or when anhydrous at 191° , has $[\alpha]_D - 198.75^\circ$, and is hydrolysed by emulsin to dextrose and gentiogenin. When neutralised with potassium hydroxide or baryta, gentiopicroin forms the salts $C_{16}H_{21}O_{10}K$ and $(C_{16}H_{21}O_{10})_2Ba$ respectively, and when heated with acetic anhydride and zinc chloride it yields a *penta-acetyl* derivative, $C_{16}H_{15}O_4(OAc)_5$, which melts at 139° and has $[\alpha]_D - 164^\circ$. G. Y.

Myristicin. II. ENRICO RIMINI (*Gazzetta*, 1905, 35, i, 406—416. Compare this vol., i, 198).—The action of nitrous acid on *isomyristicin* yields (1) *isomyristicin nitrosite*, $C_{11}H_{12}O_6N_2$, which separates in yellowish-white clots, melting and decomposing at $130-131^\circ$; (2) *isomyristicin nitrosate*, $C_{11}H_{12}O_7N_2$, which crystallises from ether in orange-yellow plates, melting and decomposing slightly at 147° .

β -Nitroisomyristicin, $OMe \cdot C_6H_2(CH_2O_2) \cdot CH : CMe \cdot NO_2$, obtained by boiling *isomyristicin nitrosite*, suspended in alcohol, with piperidine, crystallises from alcohol in golden-yellow, long, silky needles melting at 112° . On boiling its alcoholic solution with hydroxylamine hydrochloride and alkali, it yields *myristicin aldoxime*, $C_9H_9O_4N$, which crystallises from alcohol in minute needles, melting at 158° . *Dibromo- β -nitroisomyristicin*, $OMe \cdot C_6H_2Br_2(CH_2O_2) \cdot CH : CMe \cdot NO_2$, crystallises from alcohol in yellowish-white plates melting at 160° ; with hydroxylamine, it yields nitroethane and *dibromomyristicin aldoxime*, $C_9H_7O_4NBr_2$, which softens at about 180° and melts at $184-186^\circ$.

When diisositroisomyristicin (*loc. cit.*) is boiled with 20 per cent. sulphuric acid solution, it yields *isomyristicin diketone monoxime*, $C_{11}H_{11}O_5N$, which crystallises from benzene in mammillary masses melting at 154° . If to the action of 20 per cent. sulphuric acid is added that of a current of steam, diisositroisomyristicin yields *isomyristicin diketone*, $C_{10}H_{10}O_3$, which crystallises from water in long, lemon-yellow needles melting at 45° , is readily soluble in alcohol, and gives a *disemicarbazone*, forming a heavy, white powder melting and decomposing at $235-236^\circ$.

On heating the above diketone monoxime with acetic anhydride and neutralising the product with sodium carbonate, it gives *myristicyldi-acetylamine*, $OMe \cdot C_6H_2(CH_2O_2) \cdot CO \cdot NAc_2$, which separates from alcohol in minute, whitish-yellow needles melting at 143° , and is decomposed by sodium hydroxide solution, yielding ammonia and myristicinic and acetic acids.

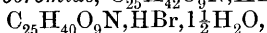
T. H. P.

Dimroth's Thiophen Dimeric Hydroxyacetate. CARL SCHWALBE (*Ber.*, 1905, 38, 2208—2210. Compare Dimroth, *Abstr.*, 1899, i, 428).—The compound described by Dimroth as thiophen dimeric hydroxyacetate contains much less sulphur than would correspond with the formula attributed to it; its formation cannot be used as an accurate means of estimating thiophen in benzene as results are obtained far in excess of the actual amount. It is probably not a definite substance, but a mixture.

W. A. D.

Aconitine. II. HEINRICH SCHULZE (*Chem. Centr.*, 1905, i, 1709; from *Apoth.-Zeit.*, 20, 368—369).—Aconine, obtained from the hydro-

chloride by means of sodium carbonate, forms an almost colourless, resinous mass, or a loose, white, rather hygroscopic powder. The temperature at which it melts varies very much with the speed at which it is heated. The *hydrobromide*, $C_{25}H_{42}O_9N, HBr, 1\frac{1}{2}H_2O$ or



forms rather large, lustrous crystals. The nitrate and sulphate have not been obtained in a crystalline form, and attempts to prepare a nitrosoamine failed. Aconine does not react with hydroxylamine, formaldehyde, or phenylhydrazine; phenylcarbimide yields an amorphous product, which is not homogeneous. The alkaloid contains four methoxy-groups and a methyl group which is combined with nitrogen; the latter can be split off by Herzig and Meyer's method. Attempts to prepare a methyl derivative by means of methyl iodide or sulphate failed; a phenol-hydroxyl group does not appear to be contained in the molecule. *Tetra-acetylaconine*, $C_{33}H_{40}O_{13}N$ or $C_{33}H_{47}O_{13}N$, crystallises from alcohol in white needles and melts and decomposes at 230—231°. *Triacetylaconitine*, $C_{40}H_{53}O_{14}N$ or $C_{40}H_{51}O_{14}N$, crystallises from alcohol in white needles, combined together in spherical aggregates, and melts at 207—208°; the *aurichloride* forms an amorphous, canary-yellow precipitate and sinters at 140—145° without showing a definite melting point. The behaviour of aconitine towards methyl sulphate shows that the molecule not only contains two hydroxyl groups, of which the hydrogen may be replaced by an acetyl or benzoyl group, but also three more hydroxyl groups, which are probably of an alcoholic nature. Since aconine is not attacked by potassium permanganate in Willstätter's test, the molecule does not appear to contain double linkings.

E. W. W.

α -Methyltetrahydroberberine. MARTIN FREUND and FRITZ MAYER (*Ber.*, 1905, **38**, 2652—2654).— *α -Methyltetrahydroberberine*, $C_{21}H_{23}O_4N$, prepared by the electrolytic reduction in a Tafel leaden beaker (*Abstr.*, 1900, ii, 588) of α -methyldihydroberberine (this vol., i, 151) in aqueous alcoholic sulphuric acid, crystallises from alcohol in faintly coloured plates melting at 166—167° with previous softening. This compound is structurally analogous with corydaline, and as the molecule contains two asymmetric carbon atoms, it should exist in two isomerides each consisting of a pair of enantiomorphs. T. H. P.

Alkaloid Salts of Methylarsonic Acid (Arrhenalic Acid). DIOSCORIDE VITALI (*Chem. Centr.*, 1905, i, 1699—1701; from *Boll. Chim. Farm.*, **44**, 229—237, 265—273).—The methylarsonates (arrhenalates) are prepared by mixing solutions of the alkaloid sulphate (1 mol.) with disodium methylarsonate (rather more than 1 mol.) and a small quantity of water, evaporating to dryness, and extracting the finely powdered residue with boiling absolute alcohol. The salts separate on cooling or on evaporating the solution.

Anhydrous *quinine methylarsonate*, $(C_{20}H_{24}O_2N_2)_2AsO(OH)_2Me$, forms colourless, odourless crystals and has a very bitter taste; it melts and turns yellow at 139—141° and at a higher temperature becomes black and emits nauseous yellow fumes. One part of the salt is soluble in 2000 of water at 20°, in about 30 of absolute alcohol,

55 of 90 per cent. alcohol, 25 of methyl alcohol, 1000 of glycerol, 500 of acetone, or 1000 of chloroform. It is more soluble in boiling water than in cold and is practically insoluble in benzene, light petroleum, or toluene, but dissolves in acids.

Quinine hydrogen methylarsonate, $C_{20}H_{24}O_2N_2 \cdot AsO(OH)_2Me$, forms colourless, odourless crystals and has a very bitter taste; it melts and becomes brown at $151-154^\circ$ and at higher temperatures turns black and emits red vapour, which condenses to a red oil. One part dissolves in 600 of water at 19° , in about 30 of absolute alcohol, 40 of 90 per cent. alcohol, 140 of amyl alcohol, 300 of ethyl acetate, 10 of methyl alcohol, or 300 of acetone. It is almost insoluble in ether or light petroleum but dissolves in dilute acids. The aqueous solution has a faint acid reaction.

Strychnine methylarsonate, $(C_{21}H_{22}O_2N_2)_2 \cdot AsO(OH)_2Me$, forms a colourless, odourless, crystalline mass and has a bitter taste. One part dissolves in 1000 of water, in about 200 of alcohol, 500 of glycerol, or 400 of amyl alcohol; it is sparingly soluble in ethyl acetate, light petroleum, or benzene, but dissolves in dilute acids. The aqueous solution is neutral.

Strychnine hydrogen methylarsonate, $C_{21}H_{22}O_2N_2 \cdot AsO(OH)_2Me$, forms colourless, odourless crystals and has a bitter taste. One part dissolves in about 600 of water, 180 of 95 per cent. alcohol, 156 of amyl alcohol, 200 of glycerol, or 1225 of acetone. It is readily soluble in acids, but only very sparingly so in ethyl acetate and almost insoluble in ether, light petroleum, or chloroform.

A table is given showing the precipitates formed by adding solutions of the salts of some eighteen alkaloids to a 1 per cent. solution of disodium methylarsonate.

E. W. W.

Stable Quaternary Salts of Apomorphine. ROBERT PSCHORR (D.R.-P. 158620).—The quaternary salts of apomorphine, with the exception of the methiodide, are more stable and more readily crystallised than the hydrochloride hitherto employed. These salts may be prepared from apomorphine methiodide and the corresponding silver salt, or by decomposing the methiodide with moist silver oxide and adding the corresponding acid to the solution of the base thus obtained.

Apomorphine methochloride crystallises from alcohol in colourless, glistening prisms, melts at $205-210^\circ$, and dissolves readily in water or alcohol, but is insoluble in ether. The *methobromide* separates from methyl alcohol and acetone in colourless scales or six-sided plates, containing 1 mol. of acetone, and melts when dry at 180° . The methonitrate, from apomorphine and methyl nitrate, crystallises from alcohol and acetone in colourless leaflets and dissolves readily in water or alcohol (compare Abstr., 1903, i, 512).

C. H. D.

Pilocarpine and its Transformation into a New Modification. ADOLF PINNER (*Ber.*, 1905, 38, 2560—2561).—When pilocarpine hydrochloride is heated at $225-235^\circ$ for 1—2 hours, then dissolved in a little water and a 50 per cent. solution of potassium carbonate added, the oily base which separates is only partially soluble in chloroform.

The portion which is insoluble in chloroform is a new modification of pilocarpine, designated by the author as *metapilocarpine*. It differs from pilocarpine and *isopilocarpine* with respect to its salts, which are more soluble than those of its isomerides. Its *platinichloride* decomposes at 200°. By the action of strong bases on metapilocarpine or its alkyl derivative, only one nitrogen atom is eliminated as methylamine, whilst acids containing nitrogen are formed. Metapilocarpine has the formula $C_{11}H_{13}O_3N_2$. Its *hydrochloride*, *methiodide*, and *ethobromide* were prepared.

A. McK.

Symmetry of the Sparteine Molecule. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, 141, 117—119. Compare this vol., i, 608, 609).—Contrary to Scholtz and Pawlicki's statements (*Abstr.*, 1904, i, 1045), the nitrogen atoms of sparteine have the same function, and must therefore be situated symmetrically in the molecule, as the products obtained on adding either methyl iodide and hydriodic acid, or reversely hydriodic acid and methyl iodide, are identical, as are also the hydriodides of sparteine formed by addition of hydriodic acid to the free base or by elimination of methyl iodide from the hydriodide of sparteine methiodide.

The authors find that ethyl iodide does not react with sparteine methiodide at 150°, but that at 200—205° ethylene and sparteine dihydriodide are formed. Sparteine ethiodide does not enter into reaction with methyl iodide at 140°.

G. Y.

Dichloropyrrole and Dichlorodibromopyrrole. IX. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, 35, i, 477—486. Compare *Abstr.*, 1904, i, 614, 770, 771, 918, and 919).—The authors give new methods for preparing 2 : 5-dichloropyrrole and 2 : 5-dichloro-3 : 4-dibromopyrrole.

2 : 5-Dichloro-3 : 4-dibromo-1-methylpyrrole, $NMe \begin{matrix} \swarrow CCl:CBr \\ \searrow CCl:CBr \end{matrix}$, pre-

pared by the action of methyl-alcoholic potassium hydroxide and methyl iodide on a solution of 2 : 5-dichloro-3 : 4-dibromopyrrole in methyl alcohol, crystallises from alcohol in long, white needles melting at 126° and is readily soluble in light petroleum. When oxidised with concentrated nitric acid of sp. gr. 1.48, it yields dibromomaleinmethylimide.

When chlorine enters the pyrrole molecule, it first replaces the hydrogen in the 2- and 5-positions, then that in the 3- and 4-positions, and finally the iminic hydrogen.

T. H. P.

Transformations of the Nitrosopyrroles. FRANCESCO ANGELICO (*Atti Real. Accad. Lincei*, 1905, [v], 14, i, 699—703).—The action of hydroxylamine on an alkaline solution of *isonitrosopyrrole* yields an *anhydro-trioxime*, $C_4H_5O_2N_3$, which crystallises from water in shining, white needles melting and decomposing at 248—250°. The formation of this compound shows that the *isonitroso*-group of *isonitrosopyrrole* must be in the 3-position, since if it were in the 2-position a dioxime should be produced.

Similarly, 3-nitrosophenylmethylpyrrole and hydroxylamine yield the *trioxime*, $NOH:CPh \cdot C(OH) \cdot CH_2 \cdot CMe:NOH$ or $NOH:CPh \cdot CH_2 \cdot C(OH) \cdot CMe:NOH$,

which crystallises from alcohol in minute, white needles melting and decomposing at 205° , and behaves towards reagents in a manner quite analogous with that of the trioxime from nitrosodimethylpyrrole (Angelico and Calvello, Abstr., 1904, i, 447). It gives a *tribenzoyl* derivative, $C_{32}H_{25}O_6N_3$, which separates from alcohol in minute crystals melting at 156° . When heated for a short time with dilute sulphuric acid, it loses hydroxylamine, giving rise to a *compound*, $C_{11}H_{10}O_2N_2$, which crystallises from benzene in faintly yellow plates, melts at 170° , dissolves in alkalis, and forms a *benzoyl* derivative, $C_{18}H_{14}O_3N_2$, separating from alcohol in minute, white crystals melting at $158-159^{\circ}$. When subjected to the prolonged action of dilute sulphuric acid, the trioxime loses all its hydroxylamine, giving a *ketone*, $C_{11}H_9O_2N$, which crystallises from alcohol in white leaflets melting at 105° and yields a *hydrazone*, $C_{17}H_{14}O_3N_4$, crystallising from alcohol in minute, intensely yellow needles melting and decomposing at about 200° .

On heating the trioxime for a long time with water, it loses $1H_2O$, giving a *compound*, $C_{11}H_{11}O_2N_3$, which is deposited from light petroleum in small, prismatic crystals melting at 88° . Treatment of this compound with dilute sulphuric acid gives rise to a *ketone*, $C_{11}H_{10}O_2N_2$, which crystallises from light petroleum in long, white needles melting at 95° , and yields a *p-nitrophenylhydrazone*, $C_{17}H_{15}O_3N_5$, crystallising from alcohol in intensely yellow, slender needles melting and decomposing at about 202° .

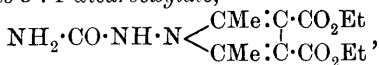
3-Nitrosodiphenylpyrrole and hydroxylamine yield (1) an *anhydrotrioxime*, $C_{16}H_{13}O_2N_3$, which separates from benzene in pale yellow, rhombic crystals melting at $141-142^{\circ}$; its *benzoyl* derivative, $C_{23}H_{17}O_3N_3$, separates from light petroleum in minute, white crystals melting at 123° ; (2) small quantities of two very characteristic compounds which are insoluble in alkalis. One of these is readily soluble in alcohol, from which it is deposited in red crystals; the other and less soluble one is yellow, but when rubbed or when boiled for a long time with alcohol it becomes converted into the red compound and passes into solution.

3-Aminotriphenylpyrrole, $C_{22}H_{18}N_2$, prepared by reducing 3-nitroso-triphenylpyrrole with either hydroxylamine or zinc dust and acetic acid, crystallises from benzene in slender, white needles melting at $184-185^{\circ}$. Its *benzoyl* derivative, $C_{29}H_{22}ON_2$, separates from benzene in minute crystals melting and decomposing at 123° . Treatment with potassium cyanate yields the corresponding *carbamide*, $C_{23}H_{19}ON_3$, which is deposited from alcohol in crystals melting and decomposing at 238° .

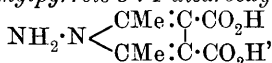
These results show that the introduction of phenyl groups retards or prevents the hydrolysis of the pyrrole ring, whilst the presence of the *isonitroso*-group favours the breaking of the ring. T. H. P.

Condensation Products of Semicarbazide and Ethyl Diacetylsuccinate. CARL BÜLOW, GUSTAV RIESS, and CONSTANTIN SAUTERMEISTER (*Ber.*, 1905, **38**, 2366—2375. Compare Abstr., 1903, i, 196; Borsche and Spannagel, Abstr., 1904, i, 779).—Ethyl diacetylsuccinate readily condenses with semicarbazide hydrochloride in the

presence of sodium acetate and acetic acid, yielding *ethyl 1-carbamido-2:5-dimethylpyrrole-3:4-dicarboxylate*,



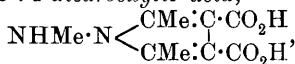
which crystallises from dilute alcohol in slender needles, melts at 202—203°, and dissolves readily in hot acetone, alcohol, or glacial acetic acid. It dissolves also in alkalis owing to the acidic properties of the imino-hydrogen atom. When hydrolysed with 15 per cent. aqueous potassium hydroxide, the ester yields the corresponding *acid*, $\text{C}_9\text{H}_{11}\text{O}_5\text{N}_3$, which crystallises from hot alcohol in microscopic needles melting at 241° and is practically insoluble in benzene, chloroform, or light petroleum. Its ammonium salt yields precipitates with solutions of silver, mercurous, mercuric, plumbous, and stannous salts. When fused at 175° with solid potassium hydroxide, the ester is converted into *1-amino-2:5-dimethylpyrrole-3:4-dicarboxylic acid*,



which crystallises from alcohol in nodular masses, melts and decomposes at 210°, and dissolves in alcohol, acetic acid, hot water, or alkalis.

When methylated with methyl sulphate in the presence of potassium hydroxide, the ester yields *ethyl 1-methylcarbamido-2:5-dimethylpyrrole-3:4-dicarboxylate*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NMe} \cdot \text{N} \begin{array}{l} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$, which

crystallises from water in glistening plates melting at 151°. When hydrolysed with 10 per cent. potassium hydroxide, the methylated ester yields the corresponding *acid*, $\text{C}_{10}\text{H}_{13}\text{O}_5\text{N}_3$, which melts and decomposes at 263°. When fused with solid potassium hydroxide at 170°, it yields alcohol, ammonia, carbon dioxide, and *1-methylamino-2:5-dimethylpyrrole-3:4-dicarboxylic acid*,



melting at 182—183°.

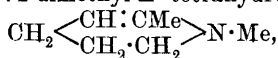
The ester of the carbamido-acid, when benzoylated by the Schotten-Baumann method, yields Bülow's ethyl 1-dibenzoylamino-2:5-dimethylpyrrole-3:4-dicarboxylate, melting at 132°, and the corresponding monobenzoyl derivative, melting at 123—124°. J. J. S.

Condensation of Nitromethane with Alkyl Derivatives of Aminomethyl Alcohol. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1905, 214—230).—As the result of a correction by Düden and the subsequent determination of the molecular weights of some of his compounds, the author acknowledges that nitromethane condenses only with two molecules of piperidylcarbinol, $\text{C}_5\text{NH}_{10} \cdot \text{CH}_2 \cdot \text{OH}$, and not with three, as previously stated by him (*ibid.*, 1896, [iii], 32, 33).

Formaldehyde condenses in aqueous alcoholic solution with one molecule of the compound $\text{NO}_2 \cdot \text{CH}(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_2$, giving rise to the substance $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_2 \cdot \text{CH}_2 \cdot \text{OH}$, which crystallises from benzene in needles melting at 101—102°; this substance may also

be obtained by the action of piperidine in aqueous solution on α -nitro-tert.-butanetriol, $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{OH})_3$. When boiled for a quarter of an hour with more piperidine, the first compound is converted into a stereoisomeric modification, which crystallises from alcohol in small needles melting at $78-79^\circ$. P. H.

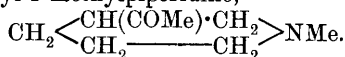
Action of Formaldehyde on 1:2-Dimethyl- Δ^2 -tetrahydropyridine, II. 3-Acetyl-1-methylpiperidine (1-Methyl-3-piperyl Methyl Ketone). ANDREAS LIPP and EDUARD WIDNMANN (*Ber.*, 1905, **38**, 2471—2482. Compare this vol., i, 610).—The formation of 1-methyl-3-ethylpiperidine by the action of formaldehyde on 1:2-dimethyl- Δ^2 -tetrahydropyridine and reduction of the product is explained by the hydrolysis of 1:2-dimethyl- Δ^2 -tetrahydropyridine,



in aqueous solution to methyl methylaminobutyl ketone,



(compare Lipp, *Abstr.*, 1896, i, 317). With formaldehyde, this forms a methylol derivative, $\text{NHMe} \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{COMe}) \cdot \text{CH}_2 \cdot \text{OH}$, which condenses to 3-acetyl-1-methylpiperidine,

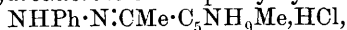


Methyl benzoylmethylaminobutyl ketone, $\text{COMe} \cdot [\text{CH}_2]_4 \cdot \text{NMeBz}$, is formed by the action of benzoyl chloride on 1:2-dimethyl- Δ^2 -tetrahydropyridine in aqueous sodium hydroxide solution. It is a colourless, viscid oil, which is not solid at -12° , is soluble in alcohol or ether, but only slightly so in water, forming an alkaline solution, and is not decomposed by evaporation with hydrochloric acid or heating with fuming hydrochloric acid at 100° ; it yields benzoic acid and 1:3-dimethyl- Δ^2 -tetrahydropyridine hydrochloride when heated with fuming hydrochloric acid in a sealed tube at $140-150^\circ$. When warmed with hydroxylamine hydrochloride and sodium carbonate in aqueous alcoholic solution, the benzoyl compound forms an *oxime*, which is obtained as a yellow oil soluble in aqueous potassium hydroxide. The phenylhydrazone of the benzoyl compound could not be purified.

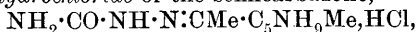
The *hydrochloride* of methyl methylaminobutyl ketoxime, formed by warming 1:2-dimethyl- Δ^2 -tetrahydropyridine with hydroxylamine hydrochloride in aqueous solution, is obtained on evaporation of its solution as a crystalline mass. The *oxime*, $\text{OH} \cdot \text{N} \cdot \text{CMe} \cdot [\text{CH}_2]_4 \cdot \text{NHMe}$, crystallises in rhombic plates, melts at $80-81^\circ$, is slightly hygroscopic, and dissolves in water to an alkaline solution. The aqueous solution of 1:2-dimethyl- Δ^2 -tetrahydropyridine reacts with semicarbazide hydrochloride to form the *hydrochloride* of methyl methylaminobutyl ketone semicarbazone, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CMe} \cdot [\text{CH}_2]_4 \cdot \text{NHMe} \cdot \text{HCl}$, which separates from alcohol in white, nodular, crystalline aggregates, melts and decomposes at 162° , has a slight acid reaction in aqueous solution, and reduces Fehling's solution when warmed. The *semicarbazone* crystallises in sheaves of needles and dissolves in water to an alkaline solution, which on warming evolves ammonia. 1:2-Dimethyl- Δ^2 -tetra-

hydropyridine reacts with phenylhydrazine in aqueous solution to form an unstable hydrazone.

The *oxime* of 3-acetyl-1-methylpiperidine, $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}_5\text{NH}_9\text{Me}$, formed by the action of hydroxylamine hydrochloride and sodium carbonate on the hydrochloride of the condensation product of formaldehyde with 1:2-dimethyl- Δ^2 -tetrahydropyridine, crystallises in small prisms, melts at $117\text{--}120^\circ$, and is soluble in aqueous potassium hydroxide. The *hydrochloride* of the phenylhydrazone,



forms glistening, granular crystals, melts and decomposes at $201\text{--}202^\circ$, and does not reduce boiling Fehling's solution; the *phenylhydrazone* is an oil. The *hydrochloride* of the semicarbazone,



crystallises in glistening plates containing $3\text{H}_2\text{O}$ and melts at 184° or, when anhydrous, with decomposition at $200\text{--}202^\circ$; the *semicarbazone* crystallises in nodular aggregates of glistening leaflets and melts at 175° .

The substance obtained by reduction of the condensation product with sodium amalgam and hydrochloric acid is 1-methyl-3- α -hydroxyethylpiperidine, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2\text{--CH}_2 \\ \text{NMe}\cdot\text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{CHMe}\cdot\text{OH}$, and not 1-methyl-2- β -hydroxyethylpiperidine as previously supposed (Abstr., 1897, i, 230); when oxidised with potassium dichromate in sulphuric acid solution, it yields 3-acetyl-1-methylpiperidine. G. Y.

Influence of Indifferent Solvents on the Alkylation of Organic Bases. NICOLAI MENSCHUTKIN (*Ber.*, 1905, 38, 2465—2466. Compare Abstr., 1895, ii, 385; 1898, i, 119; 1900, i, 341; Picner and Franz, this vol., i, 466).—A claim for priority. G. Y.

Indole Colouring Matters. MARTIN FREUND and GUSTAV LEBACH (*Ber.*, 1905, 38, 2640—2652. Compare Abstr., 1903, i, 278; 1904, i, 266).—Ehrlich found that an intensely red coloration is formed when hydrochloric acid is added to an alcoholic solution of 2-methylindole and dimethylaminobenzaldehyde. The authors find that this coloration is due to the formation of one of the rosindoles, the leuco-compounds of which are obtained by condensation of 1 mol. of an aldehyde with 2 mols. of indole or one of its derivatives with expulsion of water (compare Fischer and Wagner, Abstr., 1887, 588). For the condensation product obtained with 2-methylindole, the authors' results confirm the formula given by Fischer (Abstr., 1887, 265). It is found that in absolute alcoholic solution and in presence of hydrogen chloride, aldehydes also react in molecular proportions with 2-methylindole. The formation of the condensation products thus obtained, to which the name "*monoketoles*" is given, is explained by assuming that under these conditions 2-methylindole reacts not in the imino-form, but as indolenine. The condensation products will then be similar to the nitroso-derivatives studied by Spica and Angelico (Abstr., 1900, i, 938), and, like these, they have basic properties. Further confirmation of this constitution is furnished by the observation that condensation of 2-methylindole and an aldehyde in molecular

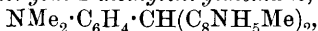
proportions does not take place when a substituent occupies the position of the hydrogen attached to the nitrogen of the indole, transformation into the indolenine form being then impossible.

On oxidation, the diketoles all yield red colouring matters. Similarly, oxidation of the monoketoles gives colouring matters which in this case almost all possess a blue tint. These compounds are obtained by digesting the monoketole in alcoholic or acetone solution with about half its weight of chloranil and a little alcoholic hydrogen chloride until no further change in colour occurs, the solution being then evaporated to dryness, and chloranil and its products of change removed from the residue by extraction with ether. The dyes are either insoluble or only very slightly soluble in water or dilute acids.

The authors suggest that the name "*indyl*" be given to the univalent indole residue, $\begin{array}{c} \text{CH}:\text{CH}\cdot\text{C}-\text{C} \\ | \quad | \\ \text{CH}:\text{CH}\cdot\text{C}\cdot\text{NH} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$, and the name "*indolenyl*-"

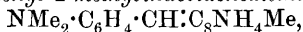
idene" or "*indolidene*" to the bivalent complex, $\begin{array}{c} \text{CH}:\text{CH}\cdot\text{C}-\text{C} \\ | \quad | \\ \text{CH}:\text{CH}\cdot\text{C}\cdot\text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$, derived from indolenine. These terms are employed in the nomenclature of the following compounds.

p-Dimethylaminophenyldi-2-methylindylmethane,



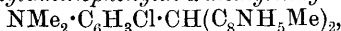
prepared from dimethylaminobenzaldehyde and 2-methylindole, crystallises from a mixture of alcohol and acetone in white needles melting at 240—242°, and is soluble in benzene or chloroform and readily so in acetone or acetic acid. On oxidation, it yields a *dye*, which forms a brownish-violet powder and dissolves in hydrochloric acid to a red solution. The dye dissolves also in alcohol or acetone, the solution being decolorised by zinc dust and hydrochloric acid; the base separated by the addition of alkali gives a brown solution in alcohol. The *methiodide*, $\text{NMe}_3\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_8\text{NH}_5\text{Me})_2$, crystallises from aqueous alcohol in white needles melting at 181—182°. The colouring matter obtained from it dyes a reddish-violet colour.

p-Dimethylaminophenyl-2-methylindolidenemethane,



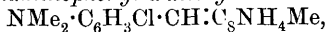
obtained from dimethylaminobenzaldehyde and 2-methylindole, separates from a mixture of acetone and water as a brownish-violet, crystalline powder softening at 295° and melting at 305°, and is readily soluble in chloroform, benzene, or acetone. The dye obtained by oxidation is a dark brown powder with a metallic reflex and is readily soluble in alcohol, the solution being decolorised by zinc dust and acetic acid. The free base obtained by the action of alkali on the dye dissolves in alcohol, giving a brown solution.

o-Chloro-*p*-dimethylaminophenyldi- α -methylindylmethane,



prepared from *o*-chloro-*p*-dimethylaminobenzaldehyde and 2-methylindole, crystallises from aqueous acetone in white needles melting at 236°. The colouring matter obtained by oxidising it dyes a reddish-violet colour.

o-Chloro-*p*-dimethylaminophenyl- α -methylindolidenemethane,



is a pale yellowish-brown substance, which sinters at 270° and melts at 282° . By means of chloranil, a bluish-violet dye is obtained.

o-Chloro-*p*-dimethylaminophenyl-di-2-methyl-1-ethylindylmethane,
 $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{CH}(\text{C}_8\text{NH}_4\text{MeEt})_2$,

crystallises from a mixture of acetone and water in slender, white needles melting at 219° , and is slightly soluble in acetic acid or acetone, and readily so in chloroform or benzene.

The authors have been unable to prepare the monoketole, $\text{CHPh} \cdot \text{C}_8\text{NH}_7$, but have separated the corresponding colouring matter as a bluish-black powder, which is soluble in alcohol giving a blue solution, and in aqueous alcoholic solution containing acetic acid dyes silk a greyish-blue colour.

o Chlorophenyl-di-2-methylindylmethane, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}(\text{C}_8\text{NH}_5\text{Me})_2$, prepared from *o*-chlorobenzaldehyde and 2-methylindole, crystallises from alcohol in white needles sintering at 230° and melting at 240° . The colouring matter obtained from it by oxidation acts as a raspberry-red dye.

o-Chlorophenyl- α -methylindolidenemethane, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH} \cdot \text{C}_8\text{NH}_4\text{Me}$, crystallises from alcohol in pale brown scales having a golden lustre, and sinters at 185° and melts and decomposes at 194 — 195° .

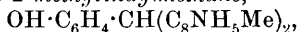
o-Nitrophenyl-di- α -methylindylmethane, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_8\text{NH}_5\text{Me})_2$, crystallises from alcohol in pale yellow needles melting at 244° . The corresponding colouring matter is pale red with a violet tinge.

o-Nitrophenyl-2-methylindolidenemethane, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{C}_8\text{NH}_4\text{Me}$, is pale brown, melts at 210° with previous sintering, and is soluble in ether or light petroleum. The hydrochloride, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{HCl}$, separates from alcohol in pale brown crystals having a golden lustre and melting at 150° . The corresponding dye has a brown tone.

o-Nitrophenyl-di-2-methyl-1-ethylindylmethane crystallises from aqueous acetone in pale yellow needles melting at 222 — 224° , and dissolves readily in chloroform, less readily in benzene or acetic acid, and slightly in alcohol or ether. It yields a bright reddish-violet dye.

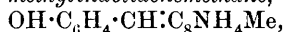
p-Nitrophenyl-di-2-methylindylmethane, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_8\text{NH}_5\text{Me})_2$, separates from alcohol in yellow crystals melting at 238° and dissolves readily in acetone. The corresponding dye is reddish-violet.

m-Hydroxyphenyl-di-2-methylindylmethane,



forms crystals melting at 222° and is readily soluble in alcohol, ether, or acetone.

m-Hydroxyphenyl-2-methylindolidenemethane,



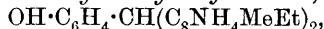
gives a hydrochloride, $\text{C}_{16}\text{H}_{14}\text{ONCl}$, which crystallises in yellowish-brown scales having a golden lustre, blackens at 160° and decomposes at 210 — 220° ; it dissolves readily in alcohol and yields a brownish-violet dye.

o-Hydroxyphenyl-di-2-methylindylmethane, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_8\text{NH}_5\text{Me})_2$, prepared from salicylaldehyde and 2-methylindole, crystallises from alcohol in needles melting at 226° and dissolving readily in acetone, chloroform, or benzene. The dye obtained from it is yellowish-red.

o-Hydroxyphenyl-2-methylindolidenemethane, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{C}_8\text{NH}_4\text{Me}$,

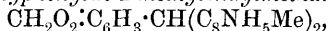
forms a yellowish powder melting at 185° and dissolving readily in alcohol. The *hydrochloride*, $C_{10}H_{13}ON, HCl$, crystallises from alcoholic hydrogen chloride in red leaflets with a golden lustre, and becomes brown at 190° and melts at 202° . The corresponding oxidation product is a violet-red dye.

o-Hydroxyphenyldi-2-methyl-1-ethylindylmethane,



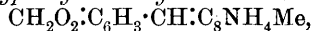
crystallises from a mixture of alcohol, acetone, and water in needles melting at 229° ; the oxidation product dyes a red colour with a faint violet tinge.

3:4-Methylenedioxyphenyldi-2-methylindylmethane,



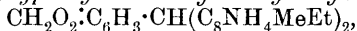
prepared from piperonaldehyde and 2-methylindole, crystallises from alcoholic acetone in needles melting and decomposing at $206-212^{\circ}$, and dissolves readily in benzene or acetic acid. The colouring matter gives a red colour with a brown tinge.

3:4-Methylenedioxyphenyl-2-methylindolenemethane,



gives a *hydrochloride* which separates from alcoholic hydrochloric acid in brown scales, darkening at 150° and decomposing at 194° , and readily soluble in acetone. The oxidation product dyes a brown colour with a violet tinge.

3:4-Methylenedioxyphenyldi-2-methyl-1-ethylindylmethane,



crystallises from aqueous acetone in needles melting at 175° , and dissolves readily in chloroform or benzene. The oxidation product acts as a vivid brownish-red dye.

Diphenyl- α -methylindolenemethane hydrochloride,



crystallises from alcohol in brown needles melting at $205-206^{\circ}$, and dyes silk an intense brown colour. By the action of alkali, the base is obtained as an oil.

T. H. P.

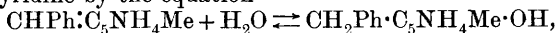
Action of Chloroform on 1:2:3-Trimethylindole. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 704—706. Compare Abstr., 1904, i, 777; and this vol., i, 298).—The action of chloroform on 1:2:3-trimethylindole in presence of sodium ethoxide yields 1:3-dimethyl-3-dichloromethyl-2-methyleneindoline, $C_6H_4 \left\langle \begin{array}{c} CMe(CHCl_2) \\ \backslash \\ NMe \end{array} \right\rangle C:CH_2$, the hydriodide of which is identical with the methiodide of 2:3-dimethyl-3-dichloromethylindolenine (*loc. cit.*).

T. H. P.

Quinoline-2-carboxylic Chloride. HANS MEYER (*Ber.*, 1905, 38, 2488—2490. Compare Abstr., 1901, i, 407; this vol., i, 155).—The melting points of pyridinecarboxylic and quinolinecarboxylic chlorides are approximately those of the hydrochlorides of the acids. These acid chlorides are insoluble in, or dissolve with decomposition in, organic solvents. The author has repeated the preparation of quinoline-2-carboxylic chloride, and finds it to melt and decompose between 168° and 175° , depending on the rate of heating; the amide

melts at 123° (Reissert, this vol., i, 472; m. p. 133°). No trace could be obtained of Besthorn and Ibele's substance melting at 97—98° (this vol., i, 612). G. Y.

Relationships of Doubly-linked Carbon to Nitrogen, Oxygen, and Sulphur. HERMANN DECKER (*Ber.*, 1905, 38, 2493—2511).—The transformation of substituted benzylidenedihydroisoquinolines into quaternary ammonium bases (Decker and Klauser, *Abstr.*, 1904, i, 338) is a general one for analogous substances where the 2-position is occupied by an alkyl or benzyl group. In the change represented for 4-benzylpyridine by the equation



the benzyl group may be replaced by an alkyl group, the nitrogen atom attached to the methyl group by oxygen or sulphur, the pyridine ring by other rings, and the alkyl group may be substituted in the 2-position instead of in the 4-position. The alkylidene bases are yellow, whilst the hydroxides are colourless. The transformations indicated are interpreted in the light of Thiele's theory of partial valencies.

Since Fosse designates as "pyrylium" compounds those derivatives of pyrone where the oxygen atom acts as a tetravalent element, the author substitutes the term "xanthylum" for the term xanthonium, formerly employed by him. "Acridan" is also substituted for dihydroacridine, "quinolan" for dihydroquinoline, "pyridan" for dihydropyridine, &c. For the hydroxydihydro-bases, the terms "acridanol," "quinolanol," "pyridanol," &c., are introduced.

[With WASLAW WISLOCKI.]—The action of magnesium benzyl chloride on 1-methyl-2-pyridone is unsuitable as a method of formation of 2-benzylidenemethylpyridan. The latter was obtained, although not isolated, owing to its instability, from 2-benzylpyridine by Tschitschibabin's method. It is orange-coloured, and is readily acted on by water to form the colourless 2-benzyl-1-methylpyridinium hydroxide, from which it is readily regenerated by the action of sodium hydroxide.

[With OSKAR KLAUSER.]—The amount of isopapaverine which could be withdrawn from a solution of papaverine bromoethoxide by means of sodium hydroxide solutions of varying concentration was quantitatively determined. The transformation of ethylisopapaverine into the corresponding quaternary ammonium base in benzene solution was also quantitatively studied.

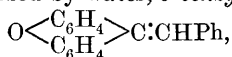
The transformation of 2-benzylquinoline methiodide into the yellow benzylidenemethylquinolan and of benzylidenemethylacridan into the ammonium salt of 10-methylacridine was examined.

5-Methylacridine, prepared from diphenylamine and acetic acid, melts at 115° and boils at 359—360° under 740 mm. pressure; its *tertiary picrate* melts at 220—221°. Its quaternary salt was prepared by the action of methyl iodide or methyl sulphate; the *quaternary methyl picrate* melts and decomposes at 199°. 5-Methylacridine methiodide could not be converted into the corresponding carbinol base.

[With HANS BÜNZLY and THEODOR VON FELLENBERG.]—*Benzyl-*

xanthylum chloride, $C_{20}H_{15}OCl$, was obtained, in admixture with benzyldiene base and carbinol, by the action of magnesium benzyl chloride on xanthone; its *ferrichloride*, $C_{20}H_{15}OCl, FeCl_3$, melts and decomposes at $148-150^\circ$; its *mercurichloride* melts at $144-146^\circ$.

Benzylxanthenol, $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle C(CH_2Ph)\cdot OH$, prepared as one of the products of the foregoing Grignard reaction, separates from light petroleum in silky needles and melts at 132° . When benzylxanthylum salts are neutralised by alkalis, or when their solutions in acid are decomposed by water, *9-benzylidenexanthen*,



is formed; it separates from alcohol in yellow needles and melts at $114-115^\circ$. *9-Benzylxanthen*, $O\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot CH_2Ph$, prepared by the action of hydriodic acid on benzylxanthenol or benzyldidenexanthen, forms glistening needles and melts at $71-72^\circ$.

When a mineral acid is added, at the ordinary temperature, to a colourless solution of benzyldidenexanthen in acetic acid, the yellowish-red colour of the xanthylum salt appears.

The *tri-iodide*, $CMe\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle OI\cdot I_2$, prepared by the action of magnesium methyl iodide on xanthone, is a violet, crystalline mass. The *ferrichloride*, $C_{14}H_{11}OCl, FeCl_3$, melts at 240° the *mercurichloride*, $C_{14}H_{11}OCl, HgCl_2$, melts at $189-190^\circ$. *9-Methylxanthenol*, $C_{14}H_{12}O_2$, forms yellow needles and melts at $96-99^\circ$.

[With THEODOR VON FELLEBERG.]—*9-Benzylthioxanthenol*, $C_{20}H_{16}OS$, prepared by the action of magnesium benzyl chloride on thioxanthone, crystallises in colourless needles and melts at 133° . On the addition of mineral acids, the red colour of the thioxanthylum salts is developed.

Benzylidenethioxanthen, $S\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle C:CHPh$, produced either as a by-product in the above Grignard reaction or by heating *9-benzylthioxanthenol*, separates from light petroleum in almost colourless needles and melts at $114-115^\circ$. Coloured thioxanthylum salts are formed by the addition of mineral acids. The *ferrichloride*, $C_{20}H_{16}SCl, FeCl_3$, prepared by the addition of ferric chloride to a solution of a benzylthioxanthylum salt, softens at 135° and melts at 155° . The *mercurichloride*, $C_{20}H_{16}SCl, HgCl_2$, melts and decomposes at $148-149^\circ$.

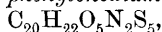
Benzylthioxanthen, $S\langle\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}\rangle CH\cdot CH_2Ph$, prepared by the action of hydriodic acid on a solution of *9-benzylthioxanthenol* in acetic anhydride, separates from alcohol in glistening needles and melts at 127° .

The action between thioxanthone and magnesium methyl iodide leads to the formation of a thioxanthylum compound, the *mercurichloride*, $C_{14}H_{11}SCl, HgCl_2$, of which melts at $156-160^\circ$.

Methylthioxanthenol methyl ether, $C_{15}H_{14}OS$, forms hexagonal plates, and melts and decomposes at $98-99^\circ$.
A. McK.

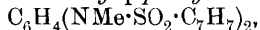
Quinonedimethylimine. (Quinonoid Compounds. IV.)

RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1905, **38**, 2244—2251. Compare *Abstr.*, 1904, i, 511, 1050; this vol., i, 361).—In the preparation of *s*-ditoluene-*p*-sulphonyl-*p*-phenylenediamine (Reverdin and Crépieux, *Abstr.*, 1901, i, 686) from toluene-*p*-sulphonic chloride and *p*-phenylenediamine, two by-products are formed in small quantity. One is *toluene-p-sulphonyl-p-phenylenediamine toluene-p-sulphonate*,



which crystallises in hard, nacreous prisms; the other is *toluene-p-sulphonyl-p-phenylenediamine*, which crystallises from dilute alcohol in needles, and melts at 183° (compare Morgan and Micklethwait, *Trans.*, 1905, **87**, 1303).

Ditoluene-p-sulphonyl-s-dimethyl-p-phenylenediamine,



prepared by methylating toluene-*p*-sulphonyl-*p*-phenylenediamine by means of methyl sulphate, crystallises from acetone in prisms, and melts at 216°. On hydrolysis with concentrated sulphuric acid, it gives *dimethyl-p-phenylenediamine*, $\text{C}_6\text{H}_4(\text{NHMe})_2$, which crystallises from light petroleum in colourless leaflets, melts at 53°, and boils at 149—150° under 17 mm. pressure; the *dihydrochloride* forms colourless needles, the *picrate* melts at 186°, and the *dinitrosoamine* forms prisms, and melts at 148°.

Methyl-*p*-phenylenediamine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$, prepared by reducing *p*-nitrosomethylaniline with tin and hydrochloric acid, forms snow-white leaflets, melts at 35·5°, and boils at 152° under 20 mm. pressure. Bernthsen and Goske (*Abstr.*, 1887, 666) described it as an uncrystallisable oil.

Quinonedimethyldi-imine, $\text{C}_6\text{H}_4(\text{NMe})_2$, prepared by oxidising *s*-dimethyl-*p*-phenylenediamine dissolved in ether with silver oxide, or, better, by oxidising the same base in light petroleum with lead peroxide, separates in colourless crystals, and melts at 92·5—93° to a dark red liquid; its solutions are coloured yellow, and it is rapidly decomposed by water or alcohol. On adding concentrated hydrochloric or sulphuric acid, it explodes; it is decomposed by hot dilute sulphuric acid, giving *p*-benzoquinone and formaldehyde.

With hydrogen chloride in ethereal solution, it gives a flocculent, reddish-brown substance which dissolves in water to an intense red solution. It does not possess the volatility of quinonedimine.

Quinonemonomethylimine, prepared by oxidising *p*-methylamino phenol (metol) with silver oxide or lead peroxide, crystallises from ether on rapid evaporation in slender needles; it is explosive and could not be analysed.

W. A. D.

Phenylhydrazine Derivatives of Aconic Acid. HANS REITTER and FRIEDRICH BENDER (*Annalen*, 1905, **339**, 373—379).—The interaction between phenylhydrazine and aconic acid (*Abstr.*, 1895, i, 128) was incorrectly interpreted; the phenylhydrazide of β -aldehydopropionic phenylhydrazone was formed thus: $\text{CO}_2\text{H}\cdot\text{C}\begin{smallmatrix} \text{CH-O} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix} + 2\text{NHPh}\cdot\text{NH}_2 = \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2\text{HPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_2\text{H}_2\text{Ph}.$

When methyl aconate is boiled in methyl-alcoholic solution with phenylhydrazine, the phenylhydrazidephenylhydrazone,
 $\text{NHPH} \cdot \text{N} : \text{CH} \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_2\text{H}_2\text{Ph}$,

of the β -monomethyl ester of γ -hydroxyitaconic acid is formed, and, as previously described, melts at 167° . At the same time, a compound, $\text{C}_{17}\text{H}_{16}\text{O}_4\text{N}_2$, is produced, and forms the main product of the reaction if the boiling is prolonged, the use of a larger quantity of methyl alcohol causing the formation only of the former; it crystallises in aggregates of needles or thin prisms melting at 186 — 190° . It is probably

a pyrazolone derivative, thus: $\text{N}_2\text{H}_2\text{Ph} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH} \begin{matrix} \text{CH} : \text{N} \\ \text{CO} - \text{NPh} \end{matrix}$.
 K. J. P. O.

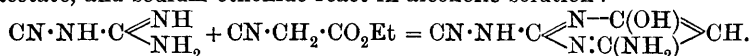
Action of Hydroxylamine Hydrochloride on Naphthaphenoxazone. FRIEDRICH KEHRMANN and H. DE GOTTRAU (*Ber.*, 1905, 38, 2574—2578).—The compound described by O. Fischer and Hepp (*Abstr.*, 1903, i, 654) as naphthaphenoxazone oxime is shown to be aminonaphthaphenoxazone, $\text{O} \begin{matrix} \text{C}_{16}\text{H}_3 : \text{N} \\ \text{O} - \text{C}_{10}\text{H}_5 \cdot \text{NH}_2 \end{matrix}$, isomeric with Kehrman and Gauhe's 2-aminophenonaphthoxazone (*Abstr.*, 1898, i, 45). The by-product obtained by Fischer and Hepp is naphtharesorufin.

The question of the quinonoid or oxonium constitution of azoxazones and also of oxazine and thiazine dyes is discussed. Hantzsch's views (this vol., i, 605) are not accepted.
 J. J. S.

Compound of Antipyrine with Mercuric Oxide. CHARLES ASTRE and JULES VILLE (*Bull. Soc. chim.*, 1905, [iii], 33, 842—845).

—The compound $\text{Hg} \left[\text{NMe}(\text{OH}) \begin{matrix} \text{CMe} : \text{CH} \\ \text{NPh} : \text{CO} \end{matrix} \right]_2$ is obtained when mercuric oxide is heated on the water-bath with an aqueous solution of antipyrine. It crystallises from absolute alcohol in short prisms melting at 195 — 196° , is only very sparingly soluble in water, ether, or benzene, and its aqueous solution has a faintly alkaline reaction. It does not give the usual reaction of mercuric salts, although it yields a black precipitate with hydrogen sulphide; it gives the usual antipyrine tests. With hydrogen chloride, it yields two definite compounds, one with 3HCl and a second with 4HCl ; the latter melts at 87 — 88° .
 J. J. S.

Cyano-derivatives of Pyrimidine. EMANUEL MERCK (D.R.-P. 158591. Compare following abstracts).—Dicyanodiamide reacts with esters of cyanoacetic, malonic, or acetoacetic acids or their derivatives to form pyrimidine derivatives. Thus dicyanodiamide, ethyl cyanoacetate, and sodium ethoxide react in alcoholic solution:



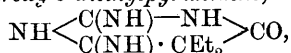
2-Cyanamino-4-amino-6-hydroxypyrimidine forms colourless crystals which decompose without melting when heated. The sodium salt is crystalline. 2-Cyanamino-6-hydroxy-4-methylpyrimidine, from dicyanodiamide and ethyl acetoacetate, forms colourless crystals and melts and

decomposes at about 265° . *2-Cyanamino-4:6-dihydroxypyrimidine*, from ethyl malonate, forms colourless crystals and decomposes when heated.

The cyano-compounds yield carboxylic acids on hydrolysis. The cyanamino-group may be replaced by oxygen, yielding barbituric acid derivatives. C. H. D.

2:4-Di-imino-6-hydroxy-5:5-dialkylpyrimidines. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158592).—Dialkylated cyanoacetic esters condense with guanidine in presence of sodium ethoxide to form pyrimidine derivatives.

2:4-Di-imino-6-hydroxy-5-diethylpyrimidine,



melts at 295° and dissolves sparingly in organic solvents or dilute alkalis, more readily in boiling water; it forms crystalline salts with strong acids. *2:4-Di-imino-6-hydroxy-5-dimethylpyrimidine* is insoluble in alcohol or ether, but dissolves readily in dilute alkalis and forms crystalline salts with acids.

The imino-groups are readily eliminated from these compounds on hydrolysis, and dialkylbarbituric acids are thus obtained. C. H. D.

Di-iminothiopyrimidine and its Alkyl Derivatives. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158621. Compare preceding abstracts).—Malononitrile and its alkyl derivatives react with thiocarbamide in presence of alkaline condensing agents, yielding di-iminothiopyrimidine and its derivatives.

4:6-Di-imino-2-thiopyrimidine, $\text{CH}_2 \begin{array}{c} \diagup \text{C}(\text{NH}) \cdot \text{NH} \diagdown \\ \diagdown \text{C}(\text{NH}) \cdot \text{NH} \diagup \end{array} \text{CS}$, from malononitrile, thiocarbamide, and alcoholic sodium ethoxide, separates from dilute acetic acid in white needles, dissolves sparingly in water or alcohol, and is insoluble in ether, benzene, or chloroform.

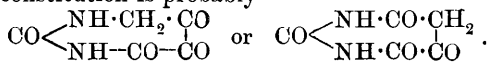
4:6-Di-imino-2-thio-5:5-diethylpyrimidine, prepared in similar manner from diethylmalononitrile, crystallises from water in yellow needles and melts and decomposes at 230° . The *dipropyl* derivative is a yellow, crystalline powder melting at 227° . The *monoethyl* derivative melts and decomposes at 292° . C. H. D.

Piperazine Monomethylarsonate. A. ASTRUC (*Bull. Soc. chim.*, 1905, [iii], 33, 839—842. Compare this vol., i, 382).—*Piperazine methylarsonate*, $[(\text{OH})_2\text{AsMeO}]_2\text{C}_4\text{H}_{10}\text{N}_2\cdot 2\text{H}_2\text{O}$, is formed when a solution of piperazine in cold alcohol is mixed with a hot alcoholic solution of methylarsonic acid. It crystallises in slender, white needles, effloresces at about $95\text{--}100^{\circ}$, loses its water of crystallisation, and then melts at 130° . It is soluble in its own weight of distilled water and the solution has an acid reaction towards phenolphthalein but basic towards Poirier-Orange No. 3. It yields precipitates with normal or basic lead acetate, silver nitrate, mercuric chloride, picric acid, or uranium acetate. J. J. S.

New Constituent of Milk. I. G. BISCARO and E. BELLONI (*Chem. Centr.*, 1905, ii, 63—64; from *Mon. Scient.*, [iv], 19, i, 384).—The

occurrence of small crystals of an organic compound in the mother liquor of lactose has led to the discovery of a new acid, orotic acid, which has been found to be a normal constituent of milk. The acid was isolated in the form of its lead salt, from which the free acid was obtained by means of hydrogen sulphide. This compound has probably hitherto escaped detection owing to the solubility of the lead salt in water. The presence of a large proportion of potassium compounds in milk in comparison with blood, urine, &c., is due to the presence of orotic acid, which has a strong affinity for potassium, which it withdraws from the tissues. *Orotic acid*, $C_5H_4O_4N_2 \cdot H_2O$, prepared by the action of sulphuric acid on the potassium salt contained in milk, forms crystals, and decomposes at 260° ; it is sparingly soluble in water and insoluble or only very slightly soluble in organic solvents. Since by the action of potassium permanganate it yields carbamide, it is probably a monoureide (compare Abstr., 1900, ii, 322). When reduced with hydrogen iodide, it forms a ketone containing the group $-CH_2 \cdot CO$. The *potassium salt*, $C_5H_3O_4N_2K$, is crystalline, and sparingly soluble in cold water. The *sodium salt*, $C_5H_3O_4N_2Na$, crystallises in large needles and, when mixed with solutions of potassium salts, forms the corresponding potassium orotate. The *silver salt*, $C_5H_3O_4N_2Ag \cdot H_2O$, prepared by adding silver nitrate to a solution of the potassium salt, forms a white, amorphous precipitate. The *normal silver salt*, $C_5H_2O_4N_2Ag_2 \cdot H_2O(?)$, obtained by adding silver nitrate to a solution of the normal potassium salt, which is prepared by heating the sodium salt with potassium hydroxide, forms a white precipitate. The *lead salt*, $C_5H_2O_4N_2Pb$, is a white precipitate and is somewhat soluble in water. E. W. W.

Orotic Acid. II. G. BISCARO and E. BELLONI (*Chem. Centr.*, 1905, ii, 64; from *Ann. Soc. Chim. Milano*, 11, 1905. Compare preceding abstract).—Orotic acid is not attacked by the lactic acid ferment nor by the process of lactic fermentation. Two *barium salts*, $(C_5H_2O_4N_2)_2Ba$ and $C_5H_2O_4N_2Ba$, are described. *Methyl orotate*, $C_5H_3O_4N_2Me$, a white, crystalline powder with a somewhat bitter taste, melts at $248-250^\circ$ and dissolves in water or alcohol, forming faintly acid solutions. *Ethyl orotate* is a white, crystalline powder, melting at 200° . *Dichloro-orotic acid*, $C_5H_4O_5N_2Cl_2 \cdot H_2O$, prepared by heating potassium orotate with phosphorus oxychloride at $160-165^\circ$, crystallises from boiling water in small, yellow needles, is soluble in ether, and melts in its water of crystallisation at 115° . It decomposes at 65° [$?165^\circ$] and at a higher temperature regenerates orotic acid with elimination of hydrogen chloride. Since the acid contains the $CO(NH)_2$ group and the group $CH_2 \cdot CO$, its constitution is probably



E. W. W.

Aliphatic Derivatives of 1:2:4-Triazole. GUIDO PELLIZZARI and ANGELO SOLDI (*Gazzetta*, 1905, 35, i, 373-388).—1-Methyl-1:2:4-triazole, $NMe \begin{array}{l} \swarrow CH:N \\ \searrow N=CH \end{array}$, prepared by the action of methyl

iodide on a methyl-alcoholic solution of sodium triazole, is a colourless liquid boiling at 178° and having the sp. gr. 1.097 at 24° ; on cooling with ice, it solidifies in large, transparent crystals melting at 20° . It is readily soluble in water, alcohol, or ether, and gives with copper sulphate in aqueous solution a blue coloration, with mercuric chloride or silver nitrate a white, crystalline precipitate, with ferric chloride a red coloration, and with oxalic and nitric acids readily soluble salts. Its *hydrochloride*, $C_3H_5N_3 \cdot HCl$, separates from a mixture of alcohol and ether as a white, deliquescent substance with no sharp melting point. The *platinichloride*, $(C_3H_5N_3)_2 \cdot H_2PtCl_6 \cdot 5H_2O$, forms orange-yellow, acicular crystals, and in the anhydrous condition melts at 165° and decomposes at a slightly higher temperature. *Tetrachloroplatinimethyltriazole*, $(C_3H_5N_3)_2PtCl_4$, obtained by the action of either hot water or heat on the platinichloride, separates in small, pale yellow, insoluble crystals. The constitution of 1-methyl-1:2:4-triazole has been settled by preparing it by the interaction of diformylmethylhydrazide and formamide.

1-*Ethyl-1:2:4-triazole*, $C_4H_7N_3$, prepared by the action of ethyl bromide on an alcoholic solution of sodium triazole, is a colourless liquid boiling at 182.5° , having the sp. gr. 1.046 at 18° and dissolving readily in water, alcohol, or ether. Its *platinichloride*, $(C_4H_7N_3)_2 \cdot H_2PtCl_6 \cdot 2H_2O$, separates in yellow, slender needles or shorter crystals melting and decomposing at $160-165^{\circ}$. *Tetrachloroplatinimethyltriazole*, $(C_4H_7N_3)_2PtCl_4$, forms microscopic, yellow crystals.

1-*Allyl-1:2:4-triazole*, $C_5H_7N_3$, is a colourless liquid boiling at 198° , having the sp. gr. 1.056 at 18° and dissolving readily in water, alcohol, or benzene. Its *platinichloride*, $(C_5H_7N_3)_2 \cdot H_2PtCl_6 \cdot H_2O$, separates from hydrochloric acid in well-formed prisms melting and decomposing at $112-115^{\circ}$. *Tetrachloroplatiniallyllyltriazole*, $(C_5H_7N_3)_2PtCl_4$, separates in canary-yellow, silky needles; if boiled for some hours with water, this compound loses a further quantity of $3HCl$, giving a compound of the composition $(C_5H_5N_3)_2PtCl_2$. T. H. P.

Action of Semicarbazide on Benzil, Benzoin, and Allied Substances. HEINRICH BILTZ (*Annalen*, 1905, 339, 243—294).—With a dilute alcoholic solution of semicarbazide, benzil yields at the ordinary temperature a monosemicarbazone, but at a higher temperature a mixture of disemicarbazone and 5:6-diphenyl-3-oxy-1:2:4-triazine. Although the acetate of the latter is probably an *O*-ester, $CPh \begin{smallmatrix} \text{CPh:N} \\ \text{N—N} \end{smallmatrix} > C \cdot OAc$, the methyl and ethyl ethers are found to be *N*-ethers, $CPh \begin{smallmatrix} \text{CPh:N} \\ \text{N—NR} \end{smallmatrix} > CO$.

The action of semicarbazide on benzoin is more complicated; at the ordinary temperature, the simple semicarbazone is formed; at higher temperatures, an additive product of oxydiphenyltriazine with 4:5-diphenyliminazolone, $\begin{smallmatrix} \text{CPh:NH} \\ | \\ \text{CPh:NH} \end{smallmatrix} > CO$, and oxydiphenyltriazine are formed according to the conditions. Anisil yields a semicarbazone and an oxytriazine, whilst anisoin gives a semicarbazone. Corresponding compounds are formed from piperil, cuminil, and cuminoin.

On reduction with zinc and acetic acid, the oxytriazines yield dihydro-oxytriazines, $\text{CPh} \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \diagdown \quad \diagup \\ \text{N} \text{---} \text{NH} \end{smallmatrix} \text{CO}$; further reduction could not be effected, but on treatment with hydriodic acid and phosphorus, ammonia and diphenyliminazolone are produced.

[With THANKMAR ARND.]—*Benzilmonosemicarbazone*, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_3$, prepared by keeping an aqueous solution of benzil, semicarbazide hydrochloride, and potassium acetate for three days, crystallises in colourless plates melting at $174\text{--}175^\circ$ and is decomposed by hydrochloric acid. When heated in alcoholic solution, the semicarbazone is converted into 3-oxy-5:6-diphenyltriazine, which crystallises in pale yellow crystals melting at $225\text{--}226^\circ$; the *sodium* derivative crystallises in pale yellow needles; the *hydrobromide* forms six-sided plates and the *nitrate* deep yellow crystals; the *hydrochloride* is unstable. The *O-acetyl* derivative crystallises in colourless prisms melting at 154° and readily hydrolysed by sodium hydroxide. 3-Oxy-5:6-diphenyl-2-methyltriazine is prepared from the triazine, methyl sulphate, and sodium methoxide in methyl alcohol, and forms colourless crystals melting and decomposing at $152\text{--}153^\circ$; it dissolves unchanged in concentrated acids. The *disemicarbazone* of benzil, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_6$, prepared by boiling benzil in diluted alcohol with semicarbazide hydrochloride and potassium acetate and removing the oxydiphenyltriazine by means of sodium hydroxide, forms leaflets melting and decomposing at $243\text{--}244^\circ$.

Benzoinsemicarbazone, $\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_3$, crystallises in prisms melting and decomposing at 206° , and on hydrolysis with hydrochloric acid yields hydrobenzoin. The *additive* product, $\text{C}_{30}\text{H}_{23}\text{O}_2\text{N}_5$, of oxydiphenyltriazine and 4:5-diphenyliminazolone is produced when benzoin in alcoholic solution is boiled with semicarbazide hydrochloride and potassium acetate for several hours, and the product crystallised from chloroform, the oxydiphenyltriazine being left in the mother liquor; it crystallises in pale yellow needles melting at $258\text{--}259^\circ$. If the potassium acetate is absent, then a substance, probably tolariedurein, which melts at 350° , together with the iminazolone and a compound melting at $247\text{--}248^\circ$, and occasionally oxydiphenyltriazine, are produced. The additive product above mentioned is decomposed into its components by heating with acetic acid, and can be again regenerated from them. 4:5-Diphenyliminazolone melts at $323\text{--}324^\circ$, fluoresces in dilute solution, and reduces ammoniacal silver solution. The *diacetyl* derivative, $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$, crystallises in needles, and the *dibenzoyl* derivative, which is formed in pyridine solution, forms colourless crystals melting at $250\text{--}251^\circ$.

[With CARL STELLBAUM.]—4:5-Diphenyliminazolone is readily prepared by heating benzoin with carbamide in acetic acid solution; the 4:5-dimethoxy-derivative, $\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_2$, prepared from anisoin and carbamide, crystallises in colourless needles melting at 284° . 4:5-Dimethylenetetraoxydiphenyliminazolone, $\text{C}_{17}\text{H}_{12}\text{O}_5\text{N}_2$, prepared from piperoïn, crystallises in needles melting at 291° . Cuminoin yields 4:5-diisopropylidiphenyliminazolone, $\text{C}_{21}\text{H}_{24}\text{ON}_2$, crystallising in needles melting at $294\text{--}295^\circ$.

[With THANKMAR ARND.]—At the ordinary temperature or on warm-

ing at 80°, semicarbazide and anisil do not react, but at 100° the disemicarbazone, $C_{18}H_{20}O_4N_6$, is produced, crystallising in leaflets melting and decomposing at 254—255°. At the same time, 3-hydroxy-

5 : 6-dimethoxydiphenyltriazine, $\begin{array}{c} OMe \cdot C_6H_4 \cdot C : N \cdot C \cdot OH \\ | \\ OMe \cdot C_6H_4 \cdot C : N \cdot N \end{array}$, is formed as

lemon-yellow prisms melting and decomposing at 261—262°. The sodium salt crystallises in yellow needles and the acetyl derivative in lemon-yellow leaflets melting and decomposing at 157°. The semicarbazone of anisoin is formed at the ordinary temperature, and crystallises in prisms melting at 185°.

Piperilmonosemicarbazone could not be prepared, but the disemicarbazone, $C_{18}H_{16}O_6N_6$, formed at 100°, crystallises in leaflets melting at 250°; at the same time, 3-hydroxy-5 : 6-dimethylenetetroxidiphenyl-

triazine, $\begin{array}{c} CH_2 : O_2 \cdot C_6H_3 \cdot C : N \cdot C \cdot OH \\ | \\ CH_2 : O_2 \cdot C_6H_3 \cdot C : N \cdot N \end{array}$, is obtained, crystallising in lemon-

yellow prisms melting at 248°. The sodium salt crystallises in yellow needles, and the acetyl derivative, $C_{19}H_{13}O_6N_3$, in orange-yellow leaflets melting and decomposing at 208°.

[With CARL STELLBAUM.]—Semicarbazide and cuminil only react at 100°, the disemicarbazone, $C_{22}H_{28}O_2N_6$, being obtained as leaflets melting and decomposing at 251—252°. 3-Hydroxy-5 : 6-diisopropyl-

diphenyltriazine, $\begin{array}{c} C_6H_4Pr^{\beta} \cdot C : N \cdot C \cdot OH \\ | \\ C_6H_4Pr^{\beta} \cdot C : N \cdot N \end{array}$, crystallises in yellow rhombo-

hedra melting at 250—251°. The acetyl derivative crystallises in yellow needles melting at 136—137°. Cuminoinsemicarbazone, $C_{21}H_{27}O_2N_3$, crystallises in needles melting and decomposing at 210°.

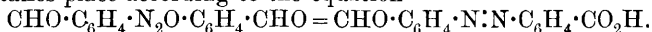
On reducing oxydiphenyltriazine with zinc foil and acetic acid, 3-oxy-5 : 6-diphenyldihydrotriazine is obtained, crystallising in needles melting at 275—276°; it is also produced by boiling benzoin and semicarbazide in dilute acetic acid solution. The diacetyl derivative forms colourless needles melting at 138°, and the dibenzoyl derivative colourless prisms melting at 188—189°. The methyl ether can only be obtained indirectly by reducing oxydiphenyltriazine methyl ether and forms crystals melting at 199°. 3-Oxy-5 : 6-dimethoxydiphenyldihydrotriazine, $C_{17}H_{17}O_3N_3$, prepared by reduction of the corresponding triazine, crystallises in needles melting at 212—213°; the diacetyl derivative crystallises in needles melting at 132°, and the dibenzoyl derivative forms crystals melting at 194—195°. 3-Oxy-5 : 6-dimethylenetetroxidiphenyldihydrotriazine, $C_{17}H_{13}O_5N_3$, prepared by reduction of oxydimethylenetetroxidiphenyltriazine, forms crystals melting at 285°. The diacetyl derivative forms crystals melting at 163° and the dibenzoyl derivative crystals melting at 212—213°. 3-Oxy-5 : 6-diisopropenyldiphenyldihydrotriazine, $C_{21}H_{25}ON_3$, prepared by reduction of the corresponding triazine or by boiling cuminoil and semicarbazide, crystallises in colourless needles melting at 255—256°; the diacetyl derivative crystallises in needles melting at 123°, and the dibenzoyl derivative forms crystals from acetone melting at 188°.

On reducing oxydiphenyldihydrotriazine with hydriodic acid and red phosphorus, 4 : 5-diphenyliminazolone is produced and forms crystals melting at 323—324°.

K. J. P. O.

A Condensation Product of Phenylmethylpyrazolone. ERNST MOHR (*Ber.*, 1905, **38**, 2578—2579).—Small quantities (10 grams) of 1-phenyl-3-methylpyrazolone distil at 191° under 17 mm. pressure without decomposing. But with larger quantities (100—150 grams) decomposition occurs, and crystals are deposited in the upper part of the flask. The amount of crystalline compound is increased by heating the pyrazolone at 250° for four hours in a reflux apparatus through which a current of dry air is passed, distilling off the more volatile products under reduced pressure, extracting the residue with about five times its weight of absolute alcohol, and then repeatedly crystallising from boiling alcohol or xylene. It has the composition $C_{20}H_{18}ON_4 = \begin{matrix} \text{CMe} \cdot \text{CH}_2 \\ | \\ \text{N} \end{matrix} \text{—NPh} > \text{C} : \text{C} < \begin{matrix} \text{CMe} \cdot \text{N} \\ | \\ \text{CO—NPh} \end{matrix}$, and crystallises in practically colourless prisms, melts at 260°, is only sparingly soluble in hot chloroform, benzene, or xylene, somewhat more readily in boiling alcohol, and readily in hot aniline or acetic acid, and possesses both basic and acidic properties. J. J. S

Transformation of Azoxybenzaldehyde. FRIEDRICH J. ALWAY and WALTER D. BONNER (*Ber.*, 1905, **38**, 2518—2520).—Human and Weil (*Abstr.*, 1904, i, 115) suppose that molecular rearrangement of *m*- and *p*-azoxybenzaldehydes by means of concentrated sulphuric acid takes place according to the equation



According to the authors, this is incorrect; the products of the transformations in question are dyes, and possess the properties characteristic of hydroxyazo-compounds. The authors further have prepared *m*-benzaldehydeazobenzoic acid and *p*-benzaldehydeazobenzoic acid, and proved that those compounds are not dyes and that they have properties different from those of the products obtained from the transformation of *m*- and *p*-azoxybenzaldehydes.

m-Benzaldehydeazobenzoic acid, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, prepared by the condensation of *m*-nitrosobenzaldehyde with *m*-aminobenzoic acid or by the hydrolysis of its ethyl ester, forms yellow needles and melts at 230° (corr.). Its *ethyl ester*, prepared from *m*-nitrosobenzaldehyde and ethyl *m*-aminobenzoate, forms reddish-yellow needles, and melts at 90° (corr.), whilst its *phenylhydrazone* melts at 195° (corr.).

The transformation product of *m*-azoxybenzaldehyde melts at 165° (corr.), is soluble with difficulty in a cold aqueous solution of sodium carbonate, and is a true dye. The *bisphenylhydrazone* melts at 234° (corr.), the *dioxime* at 207—211° (corr.), the *dianilide* at 141° (corr.), and the *monoanilide* at 126—130° with decomposition. The substance probably has the formula $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CHO}$.

p-Benzaldehydeazobenzoic acid, prepared by the condensation of *p*-nitrosobenzaldehyde with *p*-aminobenzoic acid or of *p*-aminobenzaldehyde with *p*-nitrosobenzoic acid, is a reddish-yellow powder and does not melt below 300°. The *ethyl ester* forms red crystals, and melts at 159° (corr.). A. McK.

Organic Chemistry.

Catalytic Decomposition of Alkyl Haloids by means of Anhydrous Metallic Chlorides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, 141, 238—241. Compare Abstr., 1904, i, 277, 303).—When the vapour of *isobutyl* chloride is passed over dry barium chloride heated at 300°, hydrogen chloride and *isobutylene* are produced. A small proportion of the *isobutylene* undergoes condensation to various hydrocarbons of petroleum-like odour, and it shows a tendency to recombine with the hydrogen chloride in the exit tube, forming either *isobutyl* chloride or one of its isomerides. Similar catalytic reactions take place with the vapours of ethyl, propyl, or *isoamyl* chlorides, but not with methyl chloride. These reactions also occur when barium chloride is replaced by a chloride of one of the bivalent metals, nickel, cobalt, iron, cadmium, or lead, but not with a chloride of the univalent metals, silver, potassium, or sodium. The alkyl bromides are similarly decomposed by anhydrous chlorides or bromides of the bivalent metals at 320°, and the alkyl iodides in presence of anhydrous chlorides, bromides, or iodides of the bivalent metals at temperatures above 300°.

It is suggested that in these reactions a temporary organo-metallic compound of the type $\text{BaCl} \cdot \text{C}_n\text{H}_{2n}\text{Cl}$ is formed; the latter then dissociates into the metallic chloride and the olefinic hydrocarbon.

As evidence for the view that these temporary organo-metallic derivatives are formed, it is pointed out that anhydrous aluminium chloride dissolves in *isobutyl* chloride at 0°, forming a dark liquid, which evolves butylene and hydrogen chloride, and that anhydrous ferric chloride reacts vigorously with the vapour of *isobutyl* chloride at 300°, evolving hydrogen chloride and forming a dark solid, which is regarded as being produced by the condensation of the organo-metallic compound first formed. Chromic chloride exerts no catalytic action on alkyl chlorides at 300°.

T. A. H.

Basic Properties of Oxygen: Compounds of Organic Substances containing Oxygen with Nitric, Sulphuric, and Chlorosulphonic Acids. DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1905, 27, 1013—1016. Compare Trans., 1905, 87, 784).—The following compounds of nitric acid with ether, alcohol, and acetone have been prepared by adding the acid at -50° to the organic liquid cooled to -80° .

With ethyl ether, a white compound, probably $\text{C}_4\text{H}_{10}\text{O} \cdot 2\text{HNO}_3$, is obtained which melts at -25° , and at higher temperatures undergoes oxidation. It is shown that the liquid compound prepared by Cohen and Gatecliff (*Proc.*, 1904, 20, 194) at a comparatively high temperature must have contained water.

Ethyl alcohol yields a white, crystalline compound which melts at -30° , and probably has the constitution $\text{C}_2\text{H}_6\text{O} \cdot \text{HNO}_3$. Acetone furnishes a similar compound, $\text{C}_3\text{H}_6\text{O} \cdot \text{HNO}_3$, melting at -18° .

When anhydrous sulphuric acid is added to the cooled organic substances, syrupy liquids are produced.

By the action of chlorosulphonic acid on alcohol at a low temperature, ethyl hydrogen sulphate and hydrogen chloride are formed. Ether and acetone, however, yield white, crystalline *compounds*, $2C_4H_{10}O, HClSO_3$ and $2C_3H_6O, HClSO_3$, which melt at -45° and -30° respectively. E. G.

Esterification by means of Methyl Sulphate. CARL GRAEBE (*Annalen*, 1905, 340, 244—249).—After an historical *résumé* of the observations which have been made on the preparation of methyl esters by means of methyl sulphate, an account is given of a series of experiments on the methylation of benzoic acid by this reagent.

Solutions of the salts of benzoic acid, when shaken or when heated with methyl sulphate, give but small yields of the methyl ester. If the solid salts are heated with methyl sulphate at first at 160° and finally at 205 — 210° , until distillation ceases, quantitative yields are obtained. Both the methyl groups of the methyl sulphate are used in forming the ester. Potassium benzoate gives better results than the sodium salt. Acetic acid gives exactly similar results. Tetrachlorophthalic acid is converted into its methyl ester when either a solution of its salts or the dry salt is treated with methyl sulphate. The same applies to naphthalic acid, which gives but poor yields of the ester. Chloroanilic acid can only be esterified by heating the dry potassium salt at 100° with methyl sulphate. K. J. P. O.

Reduction of Oleic Acid to Stearic Acid by Electrolysis. JULIUS PETERSEN (*Chem. Centr.*, 1905, ii, 304—305; from *Overs. K. Danske Videnskabernes Selsk. Forh.*, 1905, 137—149).—By the electrolytic reduction of oleic acid, stearic acid is formed. A good yield of the latter is obtained when a mixture of a solution of 10 grams of oleic acid in 150 c.c. of alcohol with 3 c.c. of dilute sulphuric acid is electrolysed at 32° , using a current of 1.35 amperes at about 20 volts. The cell is provided with a diaphragm and the platinum anode immersed in sulphuric acid; the cathode is of nickel gauze. The oleic acid is most readily reduced when the quantity of sulphuric acid is small. A better yield is obtained, however, when hydrochloric acid is used, and in this case 5 c.c. of a normal solution are added to 100 c.c. of the alcoholic solution of oleic acid and the mixture electrolysed with a current of 0.13 amperes. If the electrolysis is prolonged, the quantity of acid reduced decreases after a time. The longer the solution has been allowed to remain with hydrochloric acid before electrolysis the more readily is it reduced by the current, possibly owing to the formation of chlorostearic acid. In an experiment in which hydrochloric acid was added slowly, drop by drop, in order to maintain the *E.M.F.* at about 20 volts, the current being one ampere and the temperature 30 — 35° , stearic acid separated out in seven hours. Increase of current density decreases the yield, but it is not affected by variation of temperature. Solutions of alkali oleates are not conveniently electrolysed owing to the formation of froth.

E. W. W.

Ammonium Oxalate; its Formula and Stability. P. V. DUPRÉ (*Analyst*, 1905, 30, 266—273).—The salt is found to have the formula $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ under all conditions of crystallisation. When heated in ordinary air it remains stable up to a temperature of from 30° to 40° , but above this temperature water is lost very slowly. In perfectly dry air, ammonium oxalate loses water even at 12° , although but slowly, whilst at 40° the loss is complete in two days. Under a pressure of one mm. the salt loses all its water in three days at as low a temperature as 6.7° . The rate of dehydration is very nearly constant for any given temperature and approximately doubles for every rise of 10° . The vapour pressure of ammonium oxalate does not reach that of water even at a temperature of 95° , nor that of air saturated to the extent of 75 per cent. with aqueous vapour. The salt is therefore stable at all temperatures up to 95° , provided the air is not less than half saturated with moisture. W. P. S.

Acid Oxalates of Ammonium. PERCY T. WALDEN (*Amer. Chem. J.*, 1905, 34, 147—152).—An investigation of the acid oxalates of ammonium has been carried out by means of the solubility method described by Foote (*Abstr.*, 1903, i, 797). The results show that the only acid salts which can be prepared from mixtures of ammonium oxalate and oxalic acid in aqueous solution at 25° are

$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, both of which have been described by Nichols (*Chem. News*, 1870, 22, 14). The compound $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, described by Rammelsberg (*Ann. Phys. Chem.*, 1854, 93, 24), could not be obtained.

E. G.

Acid Oxalates of Lithium, Sodium, Potassium, and Cæsium and their Solubility. HARRY W. FOOTE and I. A. ANDREW (*Amer. Chem. J.*, 1905, 34, 153—164).—The stable acid oxalates of lithium, sodium, potassium, and cæsium capable of formation in aqueous solution at 25° have been studied by means of the solubility method described previously (*Abstr.*, 1903, i, 797). The results are tabulated and plotted as curves.

The only salt obtainable from lithium oxalate and oxalic acid is $\text{LiHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, which was first described by Rammelsberg (*Annalen*, 1845, 56, 221). Sodium oxalate and oxalic acid also yield but one salt, $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Graham, *Annalen*, 1839, 29, 1). In addition to the two well-known acid potassium oxalates, $\text{KH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ and KHC_2O_4 , a third salt, $2\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, has been isolated, but is formed only under a narrow range of conditions and cannot be recrystallised. *Cæsium oxalate*, $\text{Cs}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is soluble in water to the extent of 75.82 per cent. of the anhydrous salt. The following acid salts have been obtained: $\text{CsH}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$; $\text{Cs}_2\text{H}_4(\text{C}_2\text{O}_4)_3$; CsHC_2O_4 ; and $\text{Cs}_8\text{H}_6(\text{C}_2\text{O}_4)_7$. E. G.

Certain Alleged Double Oxalates. HARRY W. FOOTE and I. A. ANDREW (*Amer. Chem. J.*, 1905, 34, 164—167).—The double oxalates KNaC_2O_4 , $\text{K}(\text{NH}_4)\text{C}_2\text{O}_4$, and $(\text{NH}_4)\text{LiC}_2\text{O}_4$ have been mentioned in chemical literature, but some doubt has been expressed as to their

existence. It has now been ascertained by means of the solubility method (Abstr., 1903, i, 797) that none of these salts exists at 25°.

A large number of double oxalates of ammonium with magnesium, zinc, and cadmium have been described. An investigation of these salts has been carried out by the solubility method, and it has been found that no double oxalate is formed at 25°, and, further, that owing to the very slight solubility of magnesium, zinc, and cadmium oxalates in saturated solutions of ammonium oxalate it is very improbable that double salts of these oxalates exist at any temperature. E. G.

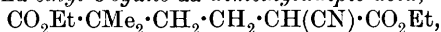
Synthesis of Dibasic Acids. I. GUSTAVE BLANC (*Bull. Soc. chim.*, 1905, [iii], 33, 879—897. Compare this vol., i, 15, 115; Bouveault and Blanc, Abstr., 1904, i, 642; this vol., i, 11).—Ethyl $\alpha\alpha$ -dimethylsuccinate and $\alpha\alpha$ -dimethylsuccinic anhydride are reduced by sodium and alcohol, the anhydride the more easily, with formation of (a) the corresponding glycol, (b) a substance which distils together with the alcohol, and could not be obtained in a state of purity; it has a burning taste, an odour resembling that of acetone, is miscible with water, and may be 3:3-dimethyltetrahydrofuran; and (c) $\alpha\alpha$ -dimethylbutyrolactone mixed with a small proportion of $\beta\beta$ -dimethylbutyrolactone. The lactones, which cannot be separated, form a colourless liquid which boils at 200—201° under the atmospheric pressure, has a penetrating odour, is soluble in much water, and is partly precipitated from its aqueous solution on addition of potassium carbonate. The barium salt of the corresponding hydroxy-acid crystallises with 15H₂O and is very soluble in water. The hydrazino-derivative, $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ | \\ \text{CH}_2 - \text{O} \end{array} > \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{NH}_2$ (compare Blaise and Luttringer, this vol., i, 329), forms small, deliquescent crystals and melts at about 50°. When the lactone mixture is heated with potassium cyanide in a sealed tube at 270° for five hours and the product hydrolysed, there is obtained $\alpha\alpha$ -dimethylglutaric acid, which melts at 85° (compare Perkin and Smith, Trans., 1902, 81, 256) and forms a β -naphthylamide melting at 149—150°, and a small quantity of $\beta\beta$ -dimethylglutaric acid which melts at 102° and forms a β -naphthylamide melting at 188—190° and less soluble in alcohol than its isomeride.

The reduction of ethyl $\alpha\alpha$ -dimethylglutarate with sodium and alcohol leads to the formation of the corresponding glycol and of $\alpha\alpha$ -dimethylvalerolactone, $\begin{array}{c} \text{CMe}_2 \cdot \text{CO} \cdot \text{O} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{array}$. This is an oily liquid, which boils at 220° under the atmospheric pressure, has a penetrating odour, and is soluble in water, from its solution in which it is partly precipitated on addition of potassium carbonate. The barium salt of the corresponding hydroxy-acid crystallises with 1½H₂O. The action of potassium cyanide on the lactone at 280° and hydrolysis of the resulting nitrile lead to the formation of $\alpha\alpha$ -dimethyladipic acid melting at 87°. No trace of the $\beta\beta$ -isomeride could be found.

α -Methylsuccinic anhydride is reduced by sodium and alcohol to α -methylbutyrolactone (Fichter and Herbrand, Abstr., 1896, i, 463),

which is an oily liquid, boiling at 200—202°. The *hydrazino*-derivative, $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \quad \quad | \\ \text{CH}_2 \text{---} \text{O} \end{array} > \text{C}(\text{OH}) \cdot \text{NH} \cdot \text{NH}_2$, crystallises in small scales and melts at 91°. α -Methylglutaric acid only was obtained on heating the lactone with potassium cyanide and hydrolysing the product.

Ethyl γ -bromo- $\alpha\alpha$ -dimethylbutyrate, $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, is formed when $\alpha\alpha$ -dimethylbutyrolactone is heated gently with phosphorus pentabromide and the product treated with alcohol. It is a colourless, mobile liquid, possessing a characteristic persistent odour, and boils at 115—116° under 23 mm. pressure. When boiled with ethyl sodio-cyanoacetate, it forms an unsaturated ester, probably ethyl dimethylvinylacetate, and *ethyl δ -cyano- $\alpha\alpha$ -dimethyladipic acid*,



which, when hydrolysed with alcoholic potassium hydroxide and evaporated to dryness with hydrochloric acid, yields the tricarboxylic acid which is obtained on oxidising dihydroisolauroic acid with sodium hypobromite. When heated at 180°, it loses carbon dioxide, forming $\alpha\alpha$ -dimethyladipic acid.

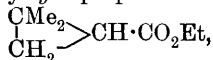
On boiling $\alpha\alpha$ -dimethyladipic acid with acetyl chloride in a reflux apparatus, the *anhydride* is obtained as a syrup (compare Tiemann, Abstr., 1901, i, 157), which, when heated at 200°, loses carbon dioxide and forms a *substance* which may be dimethylcyclopentanone. The *anilic acid*, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$, formed by heating the anhydride with aniline in benzene solution, crystallises in scales and melts at 168°.

The action of ethyl γ -bromo- $\alpha\alpha$ -dimethylbutyrate on ethyl sodio-cyanosuccinate leads to the formation of ethyl dimethylvinylacetate and the *cyano-ester*, $\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{CN})(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, which boils at 235—240° under 20 mm. pressure, and is hydrolysed easily by boiling hydrochloric acid, with formation of the *acid*, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. This crystallises in prisms, and is only slightly soluble in ether or water, but more so in alcohol. With the object of forming dihydroisolauroic acid, this tribasic acid was boiled with acetic anhydride for six hours, the acetic acid and excess of anhydride distilled off in a vacuum, and the residue heated at 240—250°, when there was obtained a viscid liquid distillate which, with semicarbazide in acetic acid solution, formed a *semicarbazone* melting at 215°. The *acid* obtained from the semicarbazone melts at 85°, is isomeric with dihydroisolauroic acid, and may have

the constitution $\begin{array}{c} \text{CMe}_2 \cdot \text{CO} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}.$ G. Y.

Synthesis of Dibasic Acids. II. GUSTAVE BLANC (*Bull. Soc. chim.*, 1905, [iii], 33, 897—911. See preceding abstract).— $\alpha\alpha$ -Dimethylvalerolactone is obtained in a yield of 25—30 per cent. of the theoretical by reducing $\alpha\alpha$ -dimethylglutaric anhydride. $\beta\beta$ -Dimethylvalerolactone, $\begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \text{---} \text{O} \end{array}$, obtained similarly by reduction of $\beta\beta$ -dimethylglutaric anhydride, forms a crystalline mass

resembling camphor, melts at 30°, and boils at 234—235°. When treated successively with potassium cyanide and hydrochloric acid, it yields $\beta\beta$ -dimethyladipic acid and a neutral *substance*, which contains 16.8 per cent. of nitrogen, crystallises in delicate spangles, and decomposes at 250°. The acid is identical with that obtained on oxidation of α -ionone, of geronic acid, and of *isogeranic acid* (Tiemann, Abstr., 1898, i, 374; Tiemann and Schmidt, *loc. cit.*, 377). When heated with a mixture of acetic anhydride and acetyl chloride, it forms the *anhydride*, $C_8H_{12}O_3$, as a viscid, colourless syrup, which with aniline in benzene solution forms an uncrystallisable *anilide*. Noyes' supposed $\beta\beta$ -dimethyladipic acid (Abstr., 1901, i, 631) is probably β -isopropylglutaric acid (compare Thorpe, Trans., 1900, 77, 942). Blaise's $\beta\beta$ -dimethylbutyrolactone (Abstr., 1898, i, 516), boiling at 208°, contains a small proportion of the *aa*-isomeride; when treated successively with phosphorus pentabromide and absolute alcohol, it forms a mixture of the γ -bromo-esters which boils at 102—104° under 9 mm. pressure and reacts with ethyl sodiocyanoacetate in absolute alcoholic solution to form ethyl 2:2-dimethylcyclopropane-1-carboxylate,



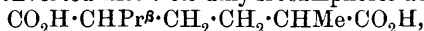
boiling at 70—80° under 9 mm. pressure, and a small quantity of the *cyano-ester*, $\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$. This boils at 175° under 8 mm. pressure, and on hydrolysis yields the *tricarboxylic acid*, which melts with evolution of carbon dioxide and formation of *aa*-dimethyladipic acid at 167°.

The product obtained on reducing α -isopropylsuccinic anhydride is a mixture of α - and β -isopropylbutyrolactones, the latter in the greater proportion. The mixture is a colourless oil which boils at 228—230°, is soluble in six times its weight of water, and forms the mixed *hydrazino*-derivatives, crystallising in small scales and melting at 95°. The corresponding *barium* salts are extremely soluble in water. The α - and β -isopropylglutaric acids formed on heating the mixed lactones with potassium cyanide and hydrolysing the nitriles so formed are separated by conversion into their anilides, of which the α -isopropylglutaranilide is much more soluble in benzene than its isomeride. These synthetical isopropylglutaric acids are racemic, whereas Martine's α -isopropylglutaric acid, as well as dihydrocamphoric acid from which it is obtained by oxidation, is optically active (compare Perkin and Crossley, Trans., 1898, 73, 23). The successive action of phosphorus pentabromide and absolute alcohol on the mixture of lactones obtained by reduction of α -isopropylsuccinic anhydride leads to the formation of a mixture of ethyl γ -bromo- α -isopropylbutyrate and its β -isopropylisomeride, which is a colourless oil boiling at 110° under 10 mm. pressure. On heating the mixture of bromo-esters with ethyl sodiocyanoacetate and distilling the product, two fractions are obtained: the first contains an *unsaturated* ester together with unchanged bromo-ester and boils at 90—95° under 10 mm. pressure; the second boils at 188—190° under 10 mm. pressure, and on hydrolysis with alcoholic potassium hydroxide and treatment with hydrochloric acid yields a considerable quantity of regenerated lactone and only very little of the *tricarboxylic acid*, $C_{10}H_{16}O_6$, melting and decomposing at

145°. It must be, therefore, a mixture of ethyl cyanoisopropyladipate and a product of the structure



Better results are obtained by condensing the γ -bromo-esters with ethyl sodiomalonate, when there are obtained the fraction mentioned previously, boiling at 90—95° under 10 mm. pressure, and the *tricarboxylic* ester, $\text{C}_{16}\text{H}_{28}\text{O}_6$, which boils at 185° under 8 mm. pressure and on hydrolysis yields the tricarboxylic acid crystallising in prisms and melting and decomposing at 145°. α -*iso*Propyladipic acid, $\text{C}_9\text{H}_{16}\text{O}_4$, formed when the tricarboxylic acid is heated at 180°, crystallises in small prisms and melts at 63°. Ethyl γ -bromo- α -isopropylbutyrate condenses with ethyl sodiomethylmalonate to form the *tricarboxylic* ester, $\text{CO}_2\text{Et}\cdot\text{CHPr}^\beta\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{CO}_2\text{Et})_2$, which boils at 188—190° under 15 mm. pressure and on hydrolysis yields the *tricarboxylic* acid, $\text{C}_{11}\text{H}_{18}\text{O}_6$. This crystallises from formic acid in small prisms, melts and decomposes at 158°, and when heated at 180° loses carbon dioxide and is converted into *r-cis*-dihydrocamphoric acid,



melting at 103°. The aqueous mother-liquors from the crystallisation of this contain a resinous isomeric acid which is probably a mixture of the *cis*- and *trans*-forms of dihydrocamphoric acid.

Campholide, which melts at 210°, and when treated with hydrogen bromide forms δ -bromocampholic acid, is obtained by reduction of camphoric acid or of its *ortho*-methyl ester, but not of the *allo*-methyl ester.

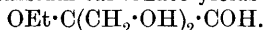
G. Y.

Action of Sodium Sulphite on Acetaldehyde. ALPHONSE SEYEWETZ and BARDIN (*Compt. rend.*, 1905, 141, 259—260).—Acetaldehyde does not react with sodium sulphite when the two reagents are mixed in dilute aqueous solution, but with concentrated solutions a vigorous action takes place, the acetaldehyde being converted into crotonaldehyde (40 per cent., compare Orndorff and Newbury, *Abstr.*, 1892, 1423, and Charon, *Abstr.*, 1896, i, 407), aldehyde resin, and a crotonic acid melting at 170—180°. The precautions to be observed in order to obtain the maximum yield of crotonaldehyde are detailed in the original.

T. A. H.

Ethoxyacetaldehyde and its Condensation Product with Formaldehyde. ALFRED KLÜGER (*Monatsh.*, 1905, 26, 879—890).—*Ethoxyacetaldehyde*, $\text{OEt}\cdot\text{CH}_2\cdot\text{COH}$, is obtained by heating ethoxyacetal with 1 mol. of water (slightly acidified by adding 2 drops of concentrated sulphuric acid to 250 c.c. of water) in acetone solution in a sealed tube at 90—95°, shaking the product with calcium chloride, and distilling. It is a transparent, mobile liquid, which boils at 71—73°, has a characteristic suffocating odour, resembling that of acetaldehyde, and reduces ammoniacal silver nitrate. An aqueous solution of ethoxyacetaldehyde is obtained by boiling ethoxyacetal with 2—3 vols. of the above slightly acidified water, in a reflux apparatus, and removing the sulphuric acid by means of barium carbonate. This solution gives the aldehyde reactions, forms silver ethoxyacetate when

boiled with silver oxide, and when treated with 2 mols. of formaldehyde in presence of potassium carbonate yields the *aldol*,



This is a viscid oil, which decomposes when warmed in air or in a vacuum, is not oxidised on exposure to air, and on reduction with aluminium amalgam yields a slightly yellow oil. The *diacetate*, $\text{OEt} \cdot \text{C}(\text{CH}_2 \cdot \text{OAc})_2 \cdot \text{COH}$, is a yellow, viscid, almost odourless oil, which boils at $172-174^\circ$ under 34 mm. pressure and reduces ammoniacal silver nitrate. G. Y.

Compounds of Ketones with Ammonia. Diethyl Ketone Ammonia. CARL THOMÆ (*Arch. Pharm.*, 1905, 243, 393—394. Compare this vol., i, 509).—When a mixture of diethyl ketone with twice its weight of alcohol is saturated with gaseous ammonia and kept for three to four weeks in the dark, the saturation with ammonia being repeated at intervals, and is then exposed in a thin layer for evaporation, an oil remains which has a composition corresponding with the formula $\text{CEt}_2(\text{N}:\text{CEt}_2)_2$. In an experiment that lasted three-quarters of a year the yield was 11 per cent. of the theoretical. From a solution of this in ether, gaseous hydrogen chloride precipitates a white, very hygroscopic salt. C. F. B.

Transformation of Dextrose into Lævulose. Detection of Lævulose. HERMANN OST (*Zeit. angew. Chem.*, 1905, 18, 1170—1178).—Dextrose is partially converted into lævulose by the prolonged action of moderately strong sulphuric acid at the ordinary temperature. The separation of calcium lævulosate is recommended for the detection of lævulose. A. McK.

Influence of Acid, Steam Pressure, and Time on the Production of Dextrose and Dextrin in the Inversion of Potato Starch by Mineral Acids. E. PAROW (*Bied. Centr.*, 1905, 34, 546—548; from *Zeit. Spiritusind.*, 1905, 121).—Starch and 0.8 per cent. of sulphuric acid under 1 atmosphere pressure yielded, after ten minutes, 16.02 per cent. of dextrose and 83.98 per cent. of dextrin; and with 1 per cent. of acid 28.94 per cent. of dextrose and 71.06 per cent. of dextrin. When the action was prolonged for twenty minutes, the amounts of dextrose were 31.06 and 47.24 per cent. with 0.8 and 1.0 per cent. of acid respectively.

Under greater pressure (1.5 and 2 atmospheres) the time is much reduced. In practice, however, a lower pressure is employed in order that the odoriferous substances present may escape. N. H. J. M.

Decomposition Products formed from Starch by Hydrolysis with Hydrochloric Acid; their Estimation in Starch-dextrose and Syrups, and their Influence on the Technical Value of Syrups. ADELBERT RÖSSING (*Chem. Zeit.*, 1905, 29, 867—873. Compare Abstr., 1904, ii, 298).—The hydrolysis of starch by means of hydrochloric acid yields, under suitable conditions, a new variety of dextrose (*δ-dextrose*), the presence of which may be detected by its undergoing a greater diminution in reducing power when treated with barium

hydroxide than normal dextrose. This diminution, which is due chiefly to the formation of lactic and other organic acids, can be used as a means of estimating dextrose in the presence of dextrin. In addition to δ -dextrose, the hydrochloric acid produces unfermentable, hygroscopic reducing substances (dextrins). The use of syrups prepared by hydrolysis with hydrochloric acid for hard sugar preparations is not to be recommended, for both the dextrose and the salts which are formed during the manufacture exert a deleterious influence, partly through their hygroscopic properties before or after melting, and partly through the inversion of sucrose consequent on the liberation of free acid. An alteration in the proportions of dextrose or dextrin has no influence on solid preparations from normal dextrose syrup.

P. H.

Tragacanth and Acacia. Comparative Viscosity of the Simple and Mixed Mucilages. EDMUND WHITE (*Pharm. J.*, 1905, [iv], 21, 133).—The viscosity of a mixture of mucilage of tragacanth and mucilage of acacia is less than that of a corresponding mixture of mucilage of tragacanth and water. This phenomenon appears to be peculiar to tragacanth and does not occur with other gums, such as ghatti, which form viscous mucilages.

E. G.

Chicle Gum. ALEXANDER TSCHIRCH and E. SCHERESCHEWSKI (*Arch. Pharm.*, 1905, 243, 378—393).—Chicle gum is obtained from *Achras sapota*, one of the *Sapotaceæ*, which grows chiefly in Mexico. The sample examined lost 2·33 per cent. when dried at 110°, and gave 4·85 per cent. ash; water dissolved 17, alcohol 60, acetone 62, ether 76, and chloroform 77 per cent. of the drug.

Nothing is present that volatilises with steam. Water extracts a gum, mixed with a little proteid substance, which was removed by means of tannic acid; the gum forms 9 per cent. of the drug; it is insoluble in alcohol, optically inactive, yields 3·76 per cent. ash, and gives the α -naphthol sulphuric acid reaction and the reactions for furfuraldehyde. No oxydase is present.

The drug was then extracted repeatedly with boiling alcohol; from the extracts, the alban crystallised on cooling. From the last extracts, γ -chicalban, $C_{15}H_{28}O$, was obtained in small quantity, equal to 0·5 per cent. of the drug; it is crystalline, and melts at 86—87°. The earlier extracts contained a small quantity, equal to 0·2 per cent. of the drug, of a substance sparingly soluble in alcohol at 50°, and melting at 219—221°; this is α -chicalban, $C_{24}H_{40}O$. The bulk of the alban consists of β -chicalban, which crystallises in a variety of forms, and seems, when purest, to form prismatic crystals or round plates which melt at 158° and have the composition $C_{18}H_{30}O$. No cinnamic or other acid was obtained by boiling either the drug or β -chicalban with alcoholic potassium hydroxide; from the alban, however, a neutral crystalline substance, $C_{24}H_{44}O$, melting at 152—153°, was isolated. By concentrating the alcoholic mother-liquor from the alban and pouring it into very dilute hydrochloric acid, chicalaftuavil, $C_{10}H_{20}O$ or $C_{10}H_{18}O$, was precipitated as a sticky, amorphous substance, which melts at 65—66° when dry; the yield was 1·5 per cent. of the drug.

The residual drug was dissolved in chloroform and the solution poured into alcohol, when *chiclagutta*, $C_{10}H_{16}$, was precipitated; this was crystallised from ether. From the chloroform-alcoholic mother-liquor, *chicalbanan* separated gradually in small amount; after recrystallising from a mixture of alcohol and ether, it melts at $55-57^{\circ}$.

It is noteworthy that, as with gutta-percha and balata, the fluavil has the lowest, the albanan the highest, percentage of carbon, the albans being intermediate. C. F. B.

Chemical Equilibrium of the System: Ammonia and Primary isoAmylamine Hydrochloride. FELIX BIDET (*Compt. rend.*, 1905, 141, 264—265. Compare Abstr., 1901, i, 634).—Dry ammonia is absorbed by primary isoamylamine hydrochloride with liberation of the amine and formation of ammonium chloride. The limiting pressures in the reaction are 105 mm. at -23° , 202 mm. at -9.5° , 262 mm. at 0° , and 452 mm. at 16° . Practically identical limiting pressures were also obtained in the inverse action, namely, the interaction of the liquid isoamylamine with solid ammonium chloride. It is probable that in these reactions the free base unites with either the ammonium chloride or the amine hydrochloride. No molecular compound of this type was isolated, but it was observed that heat is developed when primary isoamylamine (1 mol.) is added to solid primary isoamylamine hydrochloride (1 mol.). T. A. H.

Diamines. II. New Synthesis of Diamines. CARL NEUBERG [and ERNST NEIMANN] (*Zeit. physiol. Chem.*, 1905, 45, 110—120. Compare this vol., i, 158, and Curtius and Clemm, Abstr., 1901, i, 68).—*Hexamethylenediamine* ($\alpha\zeta$ -diaminohexane) is readily obtained when 1 to 3 grams of perfectly dry $\alpha\zeta$ -diaminosuberic acid are distilled from a small flask. The platinichloride, aurichloride, and a *mercurichloride*, $C_6H_{16}N_2 \cdot 2HCl \cdot 2HgCl_2$, have been prepared. *Octamethylenediamine* ($\alpha\theta$ -diamino-octane), $NH_2 \cdot [CH_2]_8 \cdot NH_2$, obtained in a similar manner from diaminosebacic acid, yields precipitates with phosphotungstic acid, tannic acid, mercuric chloride, Nessler's reagent, or potassium bismuth iodide. Only an opalescence is produced with gold chloride or picric acid in dilute solution. The *mercurichloride* has the composition $C_8H_{20}N_2 \cdot 2HgCl_2$. Lysine, when distilled, yields 7 per cent. of pentamethylenediamine, which was isolated in the form of its phenylcarbimide derivative. $\alpha\beta$ -Diaminopropionic acid yields, in a similar manner, ethylenediamine. J. J. S.

Monamino-acids obtained from Seedlings of Vicia Sativa and Lupinus Albus. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, 45, 38—60. Compare Abstr., 1902, i, 595).—The cupric salts of glycine, alanine, leucine, phenylalanine, and of tyrosine are either insoluble or extremely sparingly soluble in cold methyl alcohol, whereas cupric aminovalerate dissolves with the greatest readiness in this solvent to a blue solution. At 18° , 1 gram dissolves in 52 grams of the alcohol. This affords a simple method

for the separation of aminovaleric acid from the amino-acids mentioned above, but not from Ehrlich's *isoleucine* (Abstr., 1904, i, 560).

The amino-acids formed in seedlings of *Vicia sativa* and of *Lupinus albus* have been isolated by E. Fischer's esterification method (Abstr., 1901, i, 192) after removal of leucine and *isoleucine*. From seedlings of *V. sativa* of 8—9 days' growth, only leucine, aminovaleric acid, *isoleucine*, and phenylalanine have been isolated. From etiolated seedlings of *Lupinus albus* of 18—20 days' growth, small quantities of 2-pyrrolidinecarboxylic acid in addition to aminovaleric acid, leucine, and phenylalanine have been isolated, and probably *isoleucine* is also present.

Tryptophan (Hopkins and Cole, Abstr., 1902, i, 193; 1903, i, 590) has also been isolated from the seedlings.

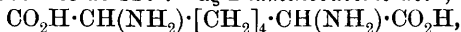
In seedlings 6 or 7 days old the amino-acid present in largest quantity is leucine, but in etiolated seedlings 2—3 weeks old the amount of this compared with aminovaleric acid and phenylalanine is comparatively small.

J. J. S.

Amino-acid obtained by the Hydrolysis of the Proteids of Lupin Seeds. ERNST WINTERSTEIN and E. PANTANELLI (*Zeit. physiol. Chem.*, 1905, 45, 61—68).—The proteids were prepared from the seeds by Ritthausen's method, hydrolysed with hydrochloric acid of sp. gr. 1.19, and the amino-acids separated by Fischer's method. The following have been isolated: alanine, aminovaleric acid, leucine, *isoleucine*, pyrrolidine-2-carboxylic acid, phenylalanine, aspartic acid, glutamic acid, and cystine. Tyrosine has been previously isolated by Schulze.

J. J. S.

Synthesis of Hydroxy- and Diamino-acids. II. Diaminosuberic Acid and Diaminosebacic Acid. CARL NEUBERG [and ERNST NEIMANN] (*Zeit. physiol. Chem.*, 1905, 45, 92—109. Compare this vol., i, 418).—Although diamino-derivatives of the lower members of the oxalic series of dibasic acids cannot readily be obtained by the action of ammonia on the corresponding dibromo-acids (Willstätter, *Ber.*, 1895, 28, 657; 1902, 35, 1379), $\alpha\zeta$ -diaminosuberic acid and $\alpha\theta$ -diaminosebacic acid are readily obtained by heating the dibromo-acids with concentrated aqueous ammonia and ammonium carbonate at 120°.



crystallises from hot ammonia, in which it is sparingly soluble, in glistening needles, and when heated above 300° sublimes and is partially decomposed into carbon dioxide and hexamethylenediamine. It dissolves in both alkalis and mineral acids. The *copper* and *silver* salts have been analysed. Precipitates are obtained when salts of most heavy metals are added to a solution of the sodium salt. The *hydrochloride*, $\text{C}_8\text{H}_{16}\text{O}_4\text{N}_2\cdot 2\text{HCl}$, is a crystalline mass, readily soluble in water, and the *phenylcarbimide* derivative, $\text{C}_{22}\text{H}_{26}\text{O}_6\text{N}_4$, crystallises from dilute alcohol in colourless needles melting at 250°.

$\alpha\theta$ -Diaminosebacic acid, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot[\text{CH}_2]_6\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, crystallises in needles, decomposes above 300°, and closely resembles the diaminosuberic acid in all respects. The *phenylcarbimide* deriv-

active melts at 210° . The *ethyl* ester distils at 240° under 10 mm. pressure, and forms a colourless oil soluble in water, alcohol, or ether, but insoluble in benzene or light petroleum; its aqueous solution has a distinct alkaline reaction and readily combines with two equivalents of acid. The *hydrochloride* crystallises in long needles soluble in water or alcohol, the *picrate*, $C_{26}H_{34}O_{18}N_8$, crystallises in sulphur-yellow needles which decompose at 198° .

The ester of diaminosuberic acid cannot be obtained by the usual method.

Both acids show a tendency to dissolve silica and alumina from porcelain vessels. J. J. S.

Synthesis of Polypeptides. XI. EMIL FISCHER (*Annalen*, 1905, 340, 123—128. Compare Abstr., 1903, i, 465, 607, 799; 1904, i, 652, 771, 867, 890; this vol., i, 30, 31, 263, 637).—In continuation of the work which has been carried out during the last two years on the synthesis of polypeptides by the action of halogen acid chlorides on amino-acids, numerous other combinations have been examined in order to obtain, if possible, compounds which take part in the building up of proteids. In addition to the halogen acids previously employed, phenylbromoacetic acid has now been used.

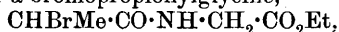
The optically active polypeptides previously described were prepared from active amino-acids; by the use of racemic acid chlorides, a mixture of active products has now been obtained, which are separated by crystallisation. On the other hand, such optically active compounds have been prepared by using optically active acid chlorides; thus an optically active alanylglycine has been prepared, which is derived from the optical antipode of the natural alanine.

When melted, the polypeptides are converted into anhydrides, the diketopiperazines, each diketopiperazine corresponding with two polypeptides; thus, glycyl-leucine and leucylglycine yield the same anhydride, *isobutyl*diketopiperazine. K. J. P. O.

Synthesis of Polypeptides. XI. Alanylglycine and Leucylalanylglycine. EMIL FISCHER and WALTER AXHAUSEN (*Annalen*, 1905, 340, 128—142).—In order to combine together the three amino-acid radicles in leucylalanylglycine, alanylglycine must first be prepared from glycine and α -bromopropionyl bromide, and then combined with α -bromohexoyl chloride; two isomeric substances are finally obtained.

α -Bromopropionylglycine, $CHBrMe \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, is prepared by treating a solution of glycine in sodium hydroxide with successive portions of bromopropionyl bromide and *N*/1 sodium hydroxide, and then evaporating the mixture to dryness under reduced pressure and extracting the residue several times with ether. The acid is precipitated with petroleum from the solution and crystallises from chloroform in aggregates of leaflets, which sinter at 100° and melt at 104° (corr.).

The *ethyl* ester of α -bromopropionylglycine,



prepared from α -bromopropionyl bromide and glycine ethyl ester in ethereal solution, crystallises in lustrous, soft needles sintering at 53° and melting at 55.5° (corr.), and is readily hydrolysed by shaking with a cold dilute solution of sodium hydroxide.

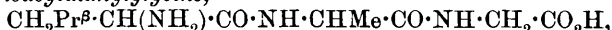
Alanylglycine, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is prepared by heating bromopropionylglycine with excess of ammonia at 100° , evaporating the solution to dryness, and dissolving the dipeptide in 50 per cent. alcohol; it crystallises in needles melting and decomposing at 235° (corr.), and has a faint acid reaction. *Carbethoxyalanylglycine*, $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, is prepared by shaking an alkaline solution of alanylglycine with ethyl chlorocarbonate and evaporating the solution to dryness after neutralising, and finally extracting with ethyl acetate; it crystallises in needles sintering at 117° and melting at 122° (corr.), and has a faint acid reaction.

α -Bromoisohexoylalaniylglycine,



is prepared by adding an excess of α -bromoisohexoyl chloride to an alkaline solution of alanylglycine and extracting the oil with ether; the product, which is a mixture of two isomerides, crystallises from water in needles and has no sharp melting point. The isomeride with the higher melting point is obtained by extracting the solid with ether and recrystallising the insoluble part from ethyl acetate; it sinters at 150° and melts at 157° (corr.); the more soluble isomeride could not be obtained in a crystalline form.

The *leucylalaniylglycine*,



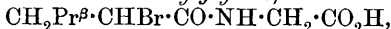
prepared by the action of ammonia on the mixed bromo-compounds, is seen to consist under the microscope of two different forms, groups of needles and prisms. *Leucylalaniylglycine* A is best obtained from the bromoisohexoylalaniylglycine melting at 154° , and melts and decomposes at 259° (corr.); it has a faint acid reaction, and is soluble in alkalis and acids. *Leucylalaniylglycine* B, prepared from the amorphous bromohexoylalaniylglycine, crystallises in thick prisms melting at 233° (corr.), but in other properties resembles the tripeptide A. The benzoyl derivative of leucylalaniylglycine A is prepared by treatment of an aqueous solution of the tripeptide with benzoyl chloride in the presence of sodium hydrogen carbonate, and crystallises with H_2O in four-sided plates or leaflets, losing water at 100° and melting at $194.5\text{--}195.5^\circ$ (corr.). The *benzoyl-leucylalaniylglycine* B crystallises from water in anhydrous, colourless needles melting at $209\text{--}210^\circ$.

Carbethoxyalanine, $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, crystallises in colourless leaflets melting at 84° (corr.); its *ethyl* ester, prepared from the ethyl ester of alanine and ethyl chlorocarbonate, crystallises in long needles melting at 25° (corr.), and is hydrolysed by shaking with a cold dilute solution of sodium hydroxide, carbethoxyalanine being formed. *Carbethoxyalanineamide*, $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH}_2$, prepared from the corresponding ester by heating with a saturated alcoholic solution of ammonia and extracting the solid left after evaporation with ethyl acetate, crystallises in short needles melting at $120\text{--}121^\circ$ (corr.). *Carbethoxyalanine chloride*, prepared from carbethoxyalanine and thionyl chloride, is unstable; dissolved in dry ether, it reacts with the

ethyl ester of glycine, yielding *carbethoxyalanylglycine ethyl ester*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which crystallises in needles melting at 67.5° (corr.), and is readily hydrolysed by alkalis. The corresponding *amide*, prepared from the ester by the action of ammonia, crystallises in needles sintering at 114° and melting at 119° (corr.).

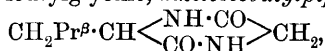
K. J. P. O.

Synthesis of Polypeptides. XI. Leucylglycine and Alanyl-leucylglycine. EMIL FISCHER and ARNOLD BRUNNER (*Annalen*, 1905, 340, 142—151).— *α -Bromoisohexoylglycine*,



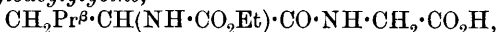
is prepared by shaking an alkaline solution of glycine with α -bromoisohexoyl chloride, and purified by crystallisation from water; it melts at 135° (corr.). When treated with aqueous ammonia, *leucylglycine* is obtained in six-sided plates melting and decomposing at 243° (corr.), and having a faint acid reaction. It forms an insoluble, deep blue, crystalline *copper salt*, $(\text{C}_8\text{H}_{15}\text{O}_3\text{N}_2\text{Cu})_2\text{O}\cdot\text{H}_2\text{O}$, which loses water under reduced pressure at 80° .

The *anhydride* of leucylglycine, *diketoisobutylpiperazine*,



prepared by heating the dipeptide at 235 — 240° , crystallises in large prisms melting at 245° (corr.), and is identical with the substance obtained by heating the ethyl ester of leucylglycine with alcoholic ammonia.

Carbethoxyleucylglycine,

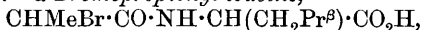


prepared from leucylglycine and ethyl chlorocarbonate, crystallises in microscopic needles sintering at 123° and melting at 127° (corr.). *Benzoyl-leucylglycine*, $\text{CH}_2\text{Pr}^\beta\cdot\text{CH}(\text{NH}\cdot\text{COPh})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, forms very long needles melting at 167° (corr.).

α -Bromopropionyl-leucylglycine, prepared from leucylglycine and α -bromopropionyl bromide, crystallises from water in anhydrous needles melting and decomposing at 165° (corr.). On keeping in contact with aqueous ammonia, the tripeptide, *alanyl-leucylglycine*, $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Pr}^\beta)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained in concentric groups of needles melting and decomposing at 232° (corr.), and has a faintly acid reaction.

K. J. P. O.

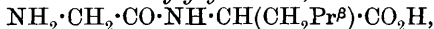
Synthesis of Polypeptides. XI. Glycyl-leucine, Alanyl-leucine, Leucylalanine, Glycylalanyl-leucine, and Active Alanylglycine. EMIL FISCHER and OTTO WARBURG (*Annalen*, 1905, 340, 152—167).— *α -Bromopropionyl-leucine*,



prepared from leucine and bromopropionyl bromide, is a mixture of two isomerides, melting at 105 — 135° , which are separated by fractional crystallisation from water; the less soluble, *α -bromopropionyl-leucine A*, forms 10 per cent. of the crude product, and crystallises in microscopic plates melting at 147 — 150° (corr.). *α -Bromopropionyl-leucine B*, which forms 50 per cent. of the crude product, melts at 113 — 118° (corr.).

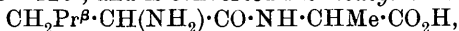
Alanyl-leucine A, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CH}_2\text{Pr}^\beta) \cdot \text{CO}_2\text{H}$, prepared from the corresponding bromopropionyl-leucine, crystallises from water in four-sided plates melting and decomposing at 248° (corr.). With phenylcarbimide, it yields a *phenylcarbamide*, which crystallises in plates melting and decomposing at 214 — 218° (corr.). *Alanyl-leucine* B resembles its isomeride very closely, but crystallises in needles; the *phenylcarbamide* crystallises in needles melting at 185 — 189° (corr.).

Chloroacetyl-leucine, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CH}_2\text{Pr}^\beta) \cdot \text{CO}_2\text{H}$, prepared from leucine and chloroacetyl chloride in alkaline solution, crystallises in rhombic plates melting at 142° (corr.). When treated with ammonia, it is converted into *glycyl-leucine*,



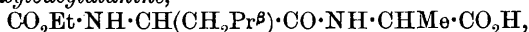
which crystallises in microscopic leaflets melting and decomposing at 242° , and gives a characteristic insoluble blue precipitate with copper sulphate, but not with other copper salts. When heated to its melting point, the dipeptide yields an anhydride which is identical with the compound obtained from leucylglycine (Fischer and Brunner, this vol., i, 690).

α -Bromoisohexoylalanine, $\text{CH}_2\text{Pr}^\beta \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, is obtained unmixed with an isomeride, crystallising in colourless leaflets melting at 123 — 126° , and is converted into *leucylalanine*,

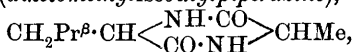


by treatment with ammonia; the dipeptide crystallises in small plates melting and decomposing at 248° (corr.), and has a faint acid reaction. In the formation of this dipeptide two by-products are obtained; the one is probably the *anhydride* of leucylalanine, and the other *isohexenoylalanine*, which would be produced by elimination of hydrogen bromide from the bromohexoyl derivative. It is isolated as a strongly acid oil, which, when heated with dilute sulphuric acid, gives an oily volatile acid resembling *α -isohexenoic acid*.

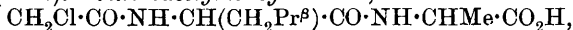
Carbethoxyleucylalanine,



crystallises in four-sided plates melting at 166 — 168° (corr.). *Leucylalanine anhydride* (*diketomethylisobutylpiperazine*),

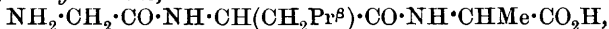


prepared by heating leucylalanine at 250° , crystallises in needles melting at 247° (corr.). *Chloroacetyl-leucylalanine*,



prepared from leucylalanine and chloroacetyl chloride, melts indistinctly at 158 — 161° (corr.).

Glycyl-leucylalanine,



crystallises in four-sided plates melting and decomposing at 250° (corr.), reddens blue litmus paper, and gives a reddish-violet coloration with alkali and a copper salt.

l-Alanylglycine, $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, was prepared by means of *l*-bromopropionyl chloride and the ethyl ester of glycine; the *ethyl ester* of *l*-bromopropionylglycine thus obtained melts at 50 — 52° , and on hydrolysis yields *l*-bromopropionylglycine, which melts 20° higher than the inactive isomeride. The dipeptide is obtained by

treating the bromopropionylglycine with aqueous ammonia at the ordinary temperature, and crystallises in tetrahedra melting and decomposing at 256° (corr.). It has in aqueous solution $[\alpha]_D - 48.6^{\circ}$ at 20° ; a small quantity of the racemic compound may be mixed with the dipeptide, but on hydrolysis with concentrated hydrochloric acid the theoretical quantity of active alanine is found.

K. J. P. O.

Synthesis of Polypeptides. XI. Optically Active α -Bromopropionic Acid. EMIL FISCHER and OTTO WARBURG (*Annalen*, 1905, **340**, 168—172).—Cinchonine, strychnine, and brucine can all be used in order to separate inactive bromopropionic acid into its active constituents; in the case of brucine the dextrorotatory acid, and in the case of strychnine the levorotatory acid, crystallises out first. *l*-Bromopropionic acid is obtained by repeated recrystallisation (15—20 times) of the cinchonine bromopropionate from water. The salt is then dissolved in dilute hydrochloric acid, and the *l*-bromopropionic acid extracted with ether and distilled under a pressure of 0.2—0.4 mm., when it boils at $70-80^{\circ}$. The pure acid is an oil of sp. gr. 1.7084 and $[\alpha]_D - 26.7^{\circ}$ at 20° . By prolonged treatment with 25 per cent. ammonia, it is converted into *l*-alanine, which has $[\alpha]_D - 9^{\circ}$.

l-Bromopropionyl chloride, prepared by the action of thionyl chloride on the acid at $55-65^{\circ}$, boils at 27° under 12 mm. pressure. *l*-Bromopropionic acid is prepared from *d*-alanine by treatment with bromine and potassium bromide in the presence of dilute sulphuric acid and passing in nitrous fumes for several hours (Walden's method). The excess of bromine is removed and the bromopropionic acid distilled under reduced pressure.

K. J. P. O.

Synthesis of Polypeptides. XI. Leucylisoserine. EMIL FISCHER and WILHELM F. KOELKER (*Annalen*, 1905, **340**, 172—180).— α -Bromoisoheptylisoserine, $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, prepared from isoserine and α -bromoisoheptyl chloride, crystallises in six-sided plates melting at $136-139^{\circ}$ (corr.), and is probably a mixture, since, when treated with ammonia, it yields a mixture of two leucylisoserines, which are separated by fractional crystallisation from water. *Leucylisoserine A*, $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, is sparingly soluble in water and crystallises in microscopic plates (with H_2O), melting and decomposing at 228° ; it has a faintly acid reaction and dissolves copper oxide. The *phenylcarbamide*,

$\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\text{Pr}^{\beta})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, crystallises in prisms melting at $176-177^{\circ}$ (corr.).

Leucylisoserine B crystallises in readily soluble anhydrous needles melting and decomposing at 234° (corr.); the *phenylcarbamide* forms prisms melting at $192-193^{\circ}$ (corr.).

Both the isomeric dipeptides, when hydrolysed with hydrochloric acid, behave in exactly the same way, yielding a mixture of leucine and isoserine.

If the two leucylisoserines are structurally isomeric, in the sense of the formulæ $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{O}\cdot\text{CH}(\text{CH}_2\cdot\text{NH}_2)\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, their reaction with

nitrous acid should be different owing to the different number of NH_2 groups. It was found that the behaviour of the two dipeptides was identical, but it was also ascertained that nitrous acid, at least in the case of dipeptides, does not sharply distinguish between amino- and imino-groups; both are attacked with the evolution of nitrogen. Experiments were carried out with α -bromoisohexoylisoserine and with hippuric acid and hippurylisoserine; the results with the compound last mentioned do not agree with Curtius' conclusion (Abstr., 1904, i, 886) that the hippuryl group is linked with oxygen. The compound has no basic properties and therefore contains no amino-group; its formula is probably $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$. K. J. P. O.

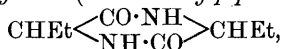
Synthesis of Polypeptides. XI. Derivatives of α -Aminobutyric Acid. EMIL FISCHER and KARL RASKE (*Annalen*, 1905, 340, 180—190).—Although α -aminobutyric acid has not hitherto been observed among the decomposition products of natural proteids, it is so nearly related to alanine and aminovaleric acid that the polypeptides derived from it have been studied.

α -Bromobutyryl chloride, $\text{CHBrEt} \cdot \text{COCl}$, prepared from α -bromobutyric acid and phosphorus pentachloride, is a heavy liquid of unpleasant odour boiling at 43° under 25 mm. pressure, and combines with glycine giving α -bromobutyrylglycine, $\text{CHBrEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, which is a crystalline solid and melts at 101 — 105° (corr.). The bromo-derivative is converted by aqueous ammonia into α -aminobutyrylglycine, which is a crystalline powder becoming brown at 200° and melting at 220° (corr.), when it changes with elimination of water into the anhydride, $\text{CHEt} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH}_2$, diketoehtylpiperazine; the latter crystallises in rhombic plates melting at 237 — 239° (corr.) and shows no basic properties.

When α -aminobutyric acid and α -bromobutyryl chloride are caused to interact, two isomeric α -bromobutyryl- α -aminobutyric acids, $\text{CHBrEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{CHEt} \cdot \text{CO}_2\text{H}$, which differ in solubility, are formed. The less soluble, the A compound, crystallises from water in small needles melting at 133° (corr.), whilst the B compound, which contributes the major quantity of the mixture, forms crystals melting at 95° (corr.).

α -Aminobutyryl- α -aminobutyric acid A, prepared from the corresponding bromo-compound, crystallises in leaflets, becoming brown at 260° and melting at 273° (corr.); it has the usual faintly acid properties; the copper salt is crystalline and sparingly soluble. The B compound, prepared from the B bromo-derivative, crystallises in microscopic needles and prisms becoming brown at 240° and melting at 257° (corr.); its soluble copper salt crystallises in microscopic prisms.

α -Aminobutyric anhydride (diketodiethylpiperazine),

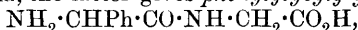


is obtained by heating both the isomeric dipeptides above their melting points and forms a crystalline mass melting at 267° ; its behaviour towards dilute acids is neutral. K. J. P. O.

Synthesis of Polypeptides. XI. Dipeptides of Phenylglycine with Glycine, Alanine, Asparagine, and Aspartic Acid. EMIL FISCHER and JULIUS SCHMIDLIN (*Annalen*, 1905, **340**, 190—204).—The phenylbromoacetic acid required for the preparation of those dipeptides which contain phenylglycine is prepared by the action of phosphorus pentabromide on mandelic acid and treatment of the resulting acid bromide with water. *Phenylbromoacetyl chloride*, $\text{CHBrPh}\cdot\text{COCl}$, prepared from the corresponding acid and phosphorus pentachloride, is a liquid boiling at $117\text{--}118^\circ$ under 18 mm. pressure; it combines with glycine yielding *phenylbromoacetylglycine*,

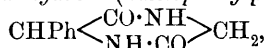


which crystallises in needles melting at $106\text{--}109^\circ$ (corr.). On treatment with ammonia, the latter gives *phenylglycylglycine*,



crystallising in leaflets melting and decomposing at 248° (corr.); its copper salt, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2\text{Cu}$, crystallises in pale blue leaflets.

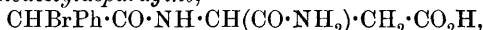
Phenylglycylglycine anhydride (diketophenylpiperazine),



prepared by heating the dipeptide above its melting point, or, better, by heating the ester of phenylglycylglycine with alcoholic ammonia, crystallises in aggregates of long needles melting and becoming coloured at 240° (corr.).

Phenylbromoacetylalanine, $\text{CHBrPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared from alanine and phenylacetyl chloride, exists in two isomeric forms, which are separated by fractional crystallisation from ethyl acetate. The A compound is the less soluble in ethyl acetate and crystallises in needles melting at $170\text{--}171^\circ$ (corr.); the B compound crystallises in short needles melting at $148\text{--}151^\circ$ (corr.). *Phenylhydroxyacetylalanine*, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is obtained by boiling both the isomeric bromo-compounds with water and crystallises in aggregates of needles melting at $142\text{--}145^\circ$ (corr.). *Phenylglycinealanine A*, $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, is prepared from the corresponding bromo-compound and crystallises in leaflets melting and decomposing at 249° ; the B compound is very sparingly soluble in water and crystallises in leaflets melting at 239° (corr.).

Phenylbromoacetylaspargine,



prepared from *L*-asparagine and phenylbromoacetyl chloride, crystallises in needles melting at $163\text{--}164^\circ$ (corr.), and has, in alkaline solution, $[\alpha]_D + 3.33^\circ$ at 20° ; the material did not appear to consist of two isomerides, as was expected. Prolonged treatment with ammonia converts the substance last mentioned into *phenylglycineasparagine*, $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises in short prisms melting at 237° (corr.) and having $[\alpha]_D - 2.3^\circ$ at 20° in alkaline solution.

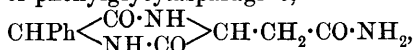
Phenylbromoacetylaspartic acid,



prepared from *L*-aspartic acid and phenylbromoacetyl chloride, is crystalline and melts at $139\text{--}143^\circ$, and has $[\alpha]_D + 3.6^\circ$ at 20° . With ammonia, a compound melting at 201° is obtained, which seems to be

an impure dipeptide. The *diethyl* ester, prepared from phenylbromoacetyl chloride and ethyl aspartate, exists only in one form, which crystallises in long needles melting at 70—71° (corr.) and has $[\alpha]_D - 13.23^\circ$ at 20°.

The *anhydride* of phenylglycylasparagine,



is prepared by heating the ester just described with a solution of ammonia in methyl alcohol; it crystallises in long prisms melting at 271° (corr.) and is easily decomposed by warm dilute sodium hydroxide. K. J. P. O.

Action of Phosphorus Pentasulphide on Carbamide and Thiocarbamide. FRANZ VON HEMMELMAYER (*Monatsh.*, 1905, 26, 765—782).—Contrary to Kutschig's statement (*Abstr.*, 1888, 1064), the product of the interaction of phosphorus pentasulphide and carbamide is *ammonium thiobiuretphosphate*, $\text{NH} \begin{array}{c} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{array} \text{PS}\cdot\text{SNH}_4$, which crystallises in monoclinic plates, decomposes at 252°, has an acid reaction in aqueous solution, evolves ammonia when heated with potassium hydroxide, gives no precipitation with magnesia mixture, and when boiled with dilute hydrochloric acid, in air or in an atmosphere of carbon dioxide, is decomposed into hydrogen sulphide, biuret, and phosphoric acid. On adding ammonia and alcohol to the aqueous solution of the primary ammonium salt, an *ammonium* salt is obtained which crystallises in glistening prisms, and on exposure to the air decomposes into ammonia and the original ammonium salt; with barium chloride in aqueous solution, the tertiary *barium* salt, $(\text{C}_2\text{H}_3\text{O}_3\text{N}_3\text{S}_2\text{P})_2\text{Ba}_3, 8\frac{1}{2}\text{H}_2\text{O}$, is obtained in glistening leaflets; it loses part of its water of crystallisation in a desiccator, has a strong alkaline reaction, and is oxidised by concentrated nitric acid or by bromine water in hydrochloric acid solution; this salt is derived from the acid $\text{NH} \begin{array}{c} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{array} \text{P}(\text{SH})_2\cdot\text{OH}$.

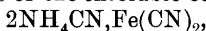
Thiobiuretphosphoric acid, $\text{NH} \begin{array}{c} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{array} \text{PS}\cdot\text{SH}, 2\text{H}_2\text{O}$, is obtained by treating the tertiary barium salt with sulphuric acid. It forms colourless, crystalline crusts, commences to decompose at 78°, changes to an opaque, white mass in a desiccator, has a strong acid reaction, and with aqueous ammonia yields the primary ammonium salt. If thiocarbamide and phosphorus pentasulphide are heated together at 130° and the product treated with water, an oil is obtained which slowly solidifies to crystals melting at about 118°; the aqueous solution contains phosphoric acid and ammonium thiocyanate. If the mixture is heated at 160°, the products are ammonium phosphate and thiocyanate and a small amount of a substance which forms large, yellow crystals and melts at 186°. G. Y.

Mercuric Zinc Cyanide. DAVID B. DOTT (*Pharm. J.*, 1905, [iv], 21, 136—137).—It has been stated by Dunstan (*Trans.*, 1892, 61,

666) that mercuric zinc cyanide, obtained by mixing solutions of mercuric cyanide, potassium cyanide, and zinc sulphate, consists of a double salt, $\text{Zn}_4\text{Hg}(\text{CN})_{10}$, mixed with a varying proportion of zinc cyanide.

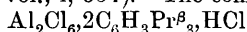
From an investigation of this precipitate, it is concluded that it has no definite composition and that the cyanide having the above formula does not exist. It is suggested that the product is a loose molecular or merely physical combination and should be termed simply "zinc and mercury cyanide." E. G.

Cyanide Mud. ADOLF HAND (*Zeit. angew. Chem.*, 1905, 18, 1098—1106).—The "cyanide mud" obtained in the recovery of cyanogen compounds from coal-gas according to Bueb's process (D.R.-P. 112459) consists of the insoluble compound,

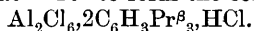


and ammonium ferrocyanide. Ammonia may be readily recovered from it. A. McK.

Compounds of Hydrogen Chloride, Hydrocarbons, and Aluminium Chloride Ferments which are formed in Friedel and Craft's Synthesis of Benzene Homologues. GABRIEL GUSTAVSON (*J. pr. Chem.*, 1905, [ii], 72, 57—79. Compare Abstr., 1903, i, 470, 804; this vol., i, 334).—The compound



is formed by mixing aluminium chloride, benzene, and isopropyl chloride in any order. The reaction takes place in two stages: on adding drop by drop a mixture of 2 mols. of benzene and 3 mols. of isopropyl chloride to aluminium chloride at 0° , the green liquid compound, $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta_3, \text{C}_6\text{H}_6$, is formed. This unites with 5 mols. of benzene to form the compound $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta_3, 6\text{C}_6\text{H}_6$, yields $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta_3$ when washed with light petroleum, is decomposed by water with formation of benzene and triisopropylbenzene, and reacts with isopropyl chloride at -10° to form the compound



When heated in a closed vessel at $65-70^\circ$, this melts and dissociates into the ferment $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta_3$, triisopropylbenzene and hydrogen chloride: these form two layers, and recombine on cooling and shaking. If the hydrogen chloride is allowed to escape at $65-70^\circ$, the two layers do not recombine, except after treatment with hydrogen chloride at -10° .

The triisopropylbenzene yields trimesic acid when oxidised with dilute nitric acid at $190-200^\circ$, and is therefore *s*-triisopropylbenzene.

The *sulphonic acid* crystallises in needles and is only sparingly soluble in water; the *barium* ($+6\text{H}_2\text{O}$), *sodium* ($+6\text{H}_2\text{O}$), and *magnesium* ($+7\text{H}_2\text{O}$) salts are described.

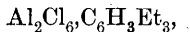
In comparison with the ethyl ferment, $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Et}_3$, the isopropyl ferment is unstable, decomposing slowly at the laboratory temperature, rapidly at 100° with evolution of a saturated gaseous hydrocarbon and the formation of a viscid, orange liquid, which, on treat-

ment with water, yields hydrocarbons which rapidly become resinous, but not triisopropylbenzene.

The compound $\text{Al}_2\text{Cl}_6, 2\text{C}_6\text{H}_3\text{Pr}^\beta, \text{HCl}$ is formed also by the action of *s*-triisopropylbenzene and hydrogen chloride on the compound $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta, \text{C}_6\text{H}_6$ at -10° , or of diisopropylbenzene and isopropyl chloride on the ferment $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta$, or of hydrogen chloride and triisopropylbenzene on aluminium chloride in presence of a small quantity of benzene. When shaken with an excess of benzene, it forms the compound $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Pr}^\beta, 6\text{C}_6\text{H}_6$, hydrogen chloride and *s*-triisopropylbenzene, the greater part of which under the influence of the ferment reacts with the excess of benzene to form isopropylbenzene.

If a current of hydrogen chloride is passed through a mixture of 1 mol. of aluminium chloride and 2 mols. of *s*-triethylbenzene, the compound $\text{Al}_2\text{Cl}_6, 2\text{C}_6\text{H}_3\text{Et}_3, \text{HCl}$ is formed as a yellow, crystalline mass, which is also obtained by passing hydrogen chloride through a mixture of the ethyl ferment, $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Et}_3$, and *s*-triethylbenzene at -8° . It melts and evolves hydrogen chloride at 50° , and when shaken with benzene dissolves with formation of two layers, the lower of which, when washed with light petroleum, yields the ethyl ferment.

The compound $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Et}_3, \text{C}_6\text{H}_3\text{Pr}^\beta, \text{HCl}$ is formed by the action of hydrogen chloride on a mixture of the ethyl ferment,



and *s*-triisopropylbenzene at -10° , or of isopropyl chloride on the compound $\text{Al}_2\text{Cl}_6, \text{C}_6\text{H}_3\text{Et}_3, \text{C}_6\text{H}_6$.

The action of *tert*.-butyl chloride and benzene on aluminium chloride at -10° leads to the formation of a yellow, crystalline compound, which is formed also by the action of *p*-di-*tert*.-butylbenzene and *tert*.-butyl chloride on powdered aluminium chloride at -10° .

tert.-Amyl chloride, benzene, and aluminium chloride react at -8° to form a liquid compound, which is formed also by the action of hydrogen chloride on a mixture of 1 mol. of aluminium chloride and 2 mols. of di-*tert*.-amylbenzene. This decomposes at the ordinary temperature with evolution of a gaseous, saturated hydrocarbon.

G. Y.

Oxidation of Aromatic Hydrocarbons by means of Cerium Peroxide. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158609).—Cerium peroxide is found to behave as a powerful oxidising agent, comparable with chromic acid, towards organic compounds in the presence of dilute acids. The crude cerium peroxide containing didymium, obtained in the manufacture of incandescent gas mantles, is suitable for the purpose. It forms a brown powder, insoluble in dilute acids, but dissolving readily in presence of aromatic hydrocarbons. Thus toluene is oxidised at 90° in 60 per cent. sulphuric acid, giving a 33 per cent. yield of benzaldehyde, together with small quantities of tolylphenylmethane and anthraquinone. Anthracene yields anthraquinone; naphthalene yields naphthaquinone or phthalic acid, according to the proportion of cerium peroxide employed. In

presence of sulphuric acid, the reaction may be so violent as to cause charring.
C. H. D.

Constitution of *as*-Di-*p*-tolylethane, 2:7:9:10-Tetramethylanthracene Dihydride, and 2:7-Dimethylantracene. JAMES LAVAUX (*Compt. rend.*, 1905, 141, 354—356).—The ditolylethane obtained by Anschütz and Romig by condensing toluene with ethylidene chloride in presence of aluminium chloride (Abstr., 1885, 768) is di-*p*-tolylethane, since it is identical with Fischer's hydrocarbon (Abstr., 1875, 154), which on oxidation yields Weiler's ditolyl ketone (Abstr., 1875, 151), and this was shown to be *p*-ditolyl ketone by Ador and Crafts (Abstr., 1878, 405). Assuming that the tetramethylantracene dihydride, simultaneously obtained by Anschütz and Romig, is produced by the further action of 1 mol. of ethylidene chloride on 1 mol. of this di-*p*-tolylethane (compare this vol., i, 43, for a similar reaction), then it can only be the 2:7:9:10-tetramethylantracene dihydride, and the product obtained by the oxidation of the latter with chromic acid (Anschütz and Romig, *loc. cit.*) must be 2:7-dimethylantraquinone. The latter is also produced by the oxidation of the B-dimethylantracene obtained by the author (this vol., i, 125); therefore this B-hydrocarbon must be 2:7-dimethylantracene, and is identical with that also obtained by Anschütz and Romig by distilling the tetramethylantracene hydride, already referred to, with zinc dust.
T. A. H.

Pyrogallol 1:3-Dimethyl Ether and 2:6-Dimethoxybenzoquinone. CARL GRAEBE and HANS HESS (*Annalen*, 1905, 340, 232—243).—The partial methylation of pyrogallol by means of methyl sulphate leads, when molecular proportions of the phenol and the alkali hydroxide are used, to a mixture of the monomethyl and dimethyl ethers with unchanged pyrogallol. The same result is obtained when methyl iodide is used.

Pyrogallol 1:3-dimethyl ether, $C_6H_3(OMe)_2 \cdot OH$ [$OMe : OH : OMe = 1 : 2 : 3$], could not be prepared in a pure state from pyrogallol, but only by heating syringic acid at $240-270^\circ$; it forms crystals melting at 54.8° and boiling at 262.7° ; the picrate crystallises in orange-yellow needles melting at 61° . The *acetyl* derivative, $C_8H_5O_2 \cdot OAc$, forms crystals melting at 53.5° . When oxidised with sodium nitrite in acid solution, the dimethyl ether is converted into cedrret.

2:6-Dimethoxybenzoquinone, $C_6H_2O_2(OMe)_2$, is best prepared by oxidising the trimethyl ether of pyrogallol with nitric acid of sp. gr. 1.2 in alcoholic solution; it melts at 255° . When treated with chlorine in chloroform solution, it is converted into 3:5-dichloro-2:6-dimethoxybenzoquinone, $C_8H_6O_4Cl_2$, which forms red crystals melting at 159° , and is identical with the β -ether obtained by Kehrmann (Abstr., 1889, 707; 1890, 136, and 1891, 903) by boiling chloroanil with methyl-alcoholic potassium hydroxide. When boiled with methyl-alcoholic alkali hydroxide, *chloromethoxydihydroxybenzoquinone*, $C_6ClO_2(OH)_2 \cdot OMe$, is obtained as red needles melting at 203° ; the corresponding chloroethoxydihydroxybenzoquinone, which was prepared by Kehrmann,

is formed when alcoholic potassium hydroxide is used. 3-Chlorodimethoxybenzoquinone, $C_6H_4O_4Cl$, is formed in the partial chlorination of dimethoxybenzoquinone in chloroform, and consists of reddish-yellow crystals melting at 148° .
K. J. P. O.

Chloronium Salts. JULIUS STIEGLITZ and EDITH E. BARNARD (*J. Amer. Chem. Soc.*, 1905, 27, 1016—1019).—Baeyer (this vol., i, 281) has described some intensely coloured salts of *p*-trichloro- and *p*-triiodo-triphenylcarbinol, and has concluded that these substances do not have the quinonoid structure, for example, $C(C_6H_4Cl)_2 \cdot C_6H_4Cl \cdot O \cdot SO_3H$, but have the constitution of carbonium salts, $C(C_6H_4Cl)_3 \cdot O \cdot SO_3H$.

It is suggested that these compounds may be chloronium salts of the structure $C(C_6H_4Cl)_2 \cdot C_6H_4 \cdot Cl \cdot O \cdot SO_3H$, and evidence is brought forward in support of this view. The opinion is expressed that the existence of true carbonium salts remains very doubtful, and that the quinonoid constitution should still be adopted for the triphenylmethane dyes.
E. G.

Formation of Aromatic Methoxy-acids and of Anisole. CARL GRAEBE (*Annalen*, 1905, 340, 204—212).—It has generally been stated that in methylation by means of methyl sulphate only one of the methyl groups is actually used, but it has been found that 1 mol. of methyl sulphate will methylate 2 mols. of phenol. The methylation takes place in two stages, the first methyl group entering rapidly in the cold, whilst the introduction of the second group occurs only slowly and at a high temperature. In the methylation of hydroxybenzoic acids, it has been found that the hydroxyl groups in the meta- and para-positions are far more readily converted into methoxyl groups than the hydroxyl group in the ortho-position relative to the carboxyl group. The same rule holds good when the methylation is effected by methyl iodide. If a mixture of *o*- and *p*- or of *o*- and *m*-hydroxybenzoic acids is treated with methyl sulphate, the meta- and para-acids are first methylated whilst the salicylic acid remains unchanged. A mixture of meta- and para-acids yields equal amounts of methyl derivative in a given time.

The methylation is best carried out by shaking a faintly alkaline aqueous solution of the phenol or hydroxy-compound with the methyl sulphate, and then adding excess of alkali and boiling.

K. J. P. O.

Specific Rotatory Powers of Tyrosine Preparations of Vegetable Origin. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, 45, 79—83. Compare Abstr., 1902, i, 595).—The following values of $[\alpha]_D$ at 20° for tyrosine prepared from various sources have been obtained. From potato -14.6° to -16.1° ; from tubers of *Dahlia variabilis* -12.9° ; by autolysis of seedlings of *Lupinus albus* -16.2° . Fischer has previously (Abstr., 1900, i, 172) found for tyrosine from casein -11.6 to -13.2° , and for a product obtained by the resolution of racemic tyrosine a value $+16.4^\circ$. The differences are attributed to the presence of small amounts of the

racemic compound in some of the specimens obtained from natural sources. All determinations were made in 4 per cent. hydrochloric acid solution.

J. J. S.

Reaction between Unsaturated Compounds and Organic Magnesium Compounds. VI. Reactions with Ethyl Benzylidenemalonate. ELMER P. KOHLER (*Amer. Chem. J.*, 1905, **34**, 132—147).—In studying the reactions between ethyl benzylidenemalonate and organic magnesium compounds, the following general method was adopted. An ethereal solution of the ester (1 mol.) was added gradually to a well-cooled solution of the magnesium compound (1 mol.), and the mixture was boiled for half an hour. The magnesium derivatives were not isolated. The esters obtained by decomposing the magnesium derivatives are easily hydrolysed, and give a good yield of the corresponding acids.

Ethyl diphenylmethylmalonate, $\text{CHPh}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$, obtained by the action of magnesium phenyl bromide on ethyl benzylidenemalonate, boils at 235—250° under 12 mm. pressure, crystallises in slender needles, melts at 63°, and is readily soluble in alcohol, ether, or carbon disulphide; the *sodium* derivative forms small, white needles. *Ethyl hydrogen diphenylmethylmalonate* crystallises in thick needles, melts at 165—166°, decomposes above 220°, and is readily soluble in ether or acetone. *Diphenylmethylmalonic acid* crystallises from water in thin plates, and from alcohol in needles, melts and decomposes at 190—192°, and is easily soluble in alcohol or ether, and moderately so in hot water; it is slowly decomposed by boiling water with formation of carbon dioxide and $\beta\beta$ -diphenylpropionic acid. *Ethyl bromodiphenylmethylmalonate*, $\text{CHPh}_2 \cdot \text{CBr}(\text{CO}_2\text{Et})_2$, separates from alcohol in large, diamond-shaped plates, melts at 79—80°, and is readily soluble in acetone or ether and fairly so in alcohol. If this ester is left in contact with potassium hydroxide for several days, *potassium α -bromo- $\beta\beta$ -diphenylpropionate* is obtained, which is decomposed by boiling water with formation of carbon dioxide, potassium bromide, and stilbene. When the ester is boiled with alcoholic potassium hydroxide, it is converted into β -phenylcinnamic acid, which is also produced by the action of boiling alcoholic potassium hydroxide on ethyl bromodiphenylmethylmalonate. *α -Bromo- $\beta\beta$ -diphenylpropionic acid*, $\text{CHPh}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$, separates in crystals from a mixture of chloroform and light petroleum, is sparingly soluble in water, and slowly undergoes decomposition in aqueous solution into carbon dioxide, hydrogen bromide, and stilbene. *Ethyl O-acetyldiphenylmethylmalonate*, $\text{CHPh}_2 \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{OAc}) \cdot \text{OEt}$, obtained by the action of acetyl chloride on the ethereal solution of the magnesium derivative, crystallises from alcohol in large, lustrous plates, melts at 92°, is readily soluble in chloroform, acetone, or hot alcohol, and is hydrolysed by alcoholic potassium hydroxide with formation of potassium acetate and ethyl diphenylmethylmalonate. When this compound is boiled with an ethereal solution of magnesium phenyl bromide, ethyl diphenylmethylmalonate and diphenylmethylcarbinol are produced. In the preparation of this acetyl derivative, a small quantity of an

oily substance is formed, which appears to be a geometrical isomeride, and yields the same products with magnesium phenyl bromide.

By the action of bromodiphenylmethane on the magnesium compound obtained from ethyl benzylidenemalonate and magnesium phenyl bromide, an *O-diphenylmethyl* derivative of ethyl diphenylmethylmalonate, $\text{CHPh}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{O}\cdot\text{CHPh}_2)\cdot\text{OEt}$, is obtained, which crystallises in plates, melts at 132° , and is readily soluble in chloroform or acetone, and moderately so in alcohol or ether; when heated with hydrochloric acid in a sealed tube at 175 — 180° for eight hours, it is decomposed into carbon dioxide, ethyl chloride, and $\beta\beta$ -diphenylpropionic acid.

Ethyl β -phenylethylmalonate, $\text{CHPhMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, prepared from ethyl benzylidenemalonate and magnesium methyl iodide, is a colourless liquid which boils at 230 — 235° under 15 mm. pressure. The corresponding *acid* crystallises in large plates, melts at 144° , is readily soluble in alcohol or ether, and moderately so in hot water, and when heated at 180° is decomposed into carbon dioxide and β -phenylbutyric acid. β -Phenylbutyric acid (Kohler and Reimer, this vol., i, 348) crystallises in large, lustrous prisms and melts at 47° .

α -Bromo- γ -phenylvaleric acid, $\text{CHPhMe}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, obtained by the addition of bromine to the product of the action of magnesium ethyl bromide on ethyl benzylidenemalonate, crystallises from a mixture of chloroform and light petroleum, melts at 176° , decomposes above 190° , and is readily soluble in alcohol, ether, or chloroform, and very slightly so in water or light petroleum. When its *potassium* salt is heated by means of a current of steam, it undergoes decomposition with formation of phenylbutylene. E. G.

Behaviour of Hydroxysalicylic Acid [Quinolcarboxylic Acid] towards Oxidising Agents. VIKTOR JUCH (*Monatsh.*, 1905, 26, 839—854. Compare Nef, *Abstr.*, 1887, 255).—Quinolcarboxylic acid is obtained in a yield of 35 per cent. of the quinol, from which it is formed by Senhofer and Sarlay's method (*Abstr.*, 1881, 1140), if xylene is used in the place of amyl alcohol. The *ethyl* ester forms almost colourless crystals and melts at 77° . On oxidation with ferric chloride in various solvents, the acid and its ester give blue to red colorations and amorphous substances which, from their odour and reaction with potassium iodide, appear to contain a small quantity of a quinone derivative.

The oxidation of quinolcarboxylic acid by manganese dioxide and concentrated sulphuric acid leads to the formation of a *product*, $\text{C}_{14}\text{H}_6\text{O}_6$, which crystallises from hot phenol or *o*-cresol as a yellow powder, melts above 360° , sublimes, with slight decomposition, in yellow, spicular prisms at 230° in a current of carbon dioxide, and when dry is stable in air. It is soluble in nitrobenzene, aniline, naphthalene, glacial acetic acid, or xylene, the solution in the last being violet by reflected and yellow by transmitted light. It dissolves in concentrated sulphuric acid to a green solution, and in aqueous alkali hydroxides or ammonia to solutions which become dark red owing to oxidation by the atmospheric oxygen. When distilled with zinc dust, it yields phenanthrene. The oxidation product

is a weak acid ; the *potassium* salt, $C_{14}H_4O_6K_2$, crystallises in glistening, delicate needles which become orange-red when dried ; the *sodium* salt crystallises from hot aqueous sodium carbonate in yellow needles. The *diacetyl* derivative, $C_{14}H_4O_6Ac_2$, crystallises in glistening, white leaflets or in needles, melts at $281-282^\circ$, commences to sublime at 200° , and is insoluble in water.

The constitution of the compound $C_{14}H_6O_6$ is discussed. G. Y.

An Oxidation Product of Homohydroxysalicylic Acid. W. DUREGGER (*Monatsh.*, 1905, **26**, 823—832. Compare Senhofer and Brunner, *Abstr.*, 1881, 265 ; Brunner, *Abstr.*, 1881, 1142).—Homohydroxysalicylic acid is oxidised by manganese dioxide and concentrated sulphuric acid to a *product*, $C_{16}H_{10}O_6$, which sublimes in long, yellow, prismatic needles, melts at about 360° , and is soluble in phenol, cresol, nitrobenzene, aniline, naphthalene, or aqueous alkali hydroxides. When distilled with zinc dust, the oxidation product yields a *hydrocarbon*, $C_{15}H_{14}$, which crystallises in white scales, melts at about 79° , and is oxidised by sodium dichromate in glacial acetic acid to a *substance* crystallising in microscopic, yellow needles and subliming at 320° . This dissolves in aqueous alkali hydroxides or carbonates, is reprecipitated by acids, and on distillation with calcium oxide yields a red liquid.

The oxidation product, $C_{16}H_{10}O_6$, is reduced by zinc dust in boiling aqueous potassium hydroxide solution to a *fluorenone* derivative, $C_{15}H_{12}O_5$, which crystallises from dilute alcohol in yellow needles, melts above 300° , dissolves in concentrated sulphuric acid to a yellow, slightly fluorescent solution, and forms a *tetra-acetyl* derivative, $C_{15}H_8O_5Ac_4$, crystallising in long, thin, white needles and melting above 300° . The fluorenone derivative is oxidised by ferric chloride or potassium dichromate in alcoholic or acetic acid solution to a *quin-hydrone* derivative, $C_{15}H_{12}O_6$, which forms dark red crystals, melts at $220-230^\circ$, and dissolves in alcohol to a red solution, which is changed to yellow by the action of sulphur dioxide. G. Y.

Methyl Ethers of Quinolcarboxylic, Protocatechuic, and Gallic Acids. CARL GRAEBE and ERNST MARTZ (*Annalen*, 1905, **340**, 213—221).—Quinolcarboxylic acid is readily prepared by oxidising salicylic acid in alkaline solution with potassium persulphate. On treatment of the acid with methyl sulphate (2 mols.) in the presence of two equivalents of sodium hydroxide, the 5-methoxy-2-hydroxybenzoic acid, which is obtained by methylation with methyl iodide, is formed ; it forms a very insoluble *calcium* salt ; its *methyl* ester, which is formed to a small extent in the formation of the ether, is readily prepared by direct methylation, and is a liquid boiling at $235-240^\circ$; this ester is alone produced if the acid is treated with methyl sulphate and only one equivalent of sodium hydroxide. The dimethyl ether is formed if the methyl sulphate is in excess, but the methylation is not complete.

Methyl quinolcarboxylate is prepared by the hydrogen chloride method, and is a solid melting at 87.8° .

Protocatechuic acid readily yields the dimethyl ether when treated

with methyl sulphate in the presence of $3\frac{1}{2}$ mols. of sodium hydroxide. In the presence of less alkali hydroxide, *isovanillic*, *vanillic*, and *veratric* acids are also produced.

Gallic acid yields a trimethyl ether readily, but on partial methylation only a monomethyl ether, the methoxyl group being in the para-position relative to the carboxyl group. Methyl gallate, on the other hand, yields the dimethyl ether, syringic acid, hydrolysis of the ester occurring in the process. Boiling of the trimethyl ether with 48 per cent. hydrobromic acid also gives this acid, which on heating yields pyrogallol 1 : 3-dimethyl ether, and on oxidation dimethoxyquinone.

K. J. P. O.

Methyleneoxyuvitic Acid. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 158716).—Paraformaldehyde reacts with a solution of hydroxyuvitic acid in concentrated sulphuric acid at the ordinary temperature. The product, *methyleneoxyuvitic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{O}-\text{CH}_2 \\ \diagup \text{CO} \cdot \text{O} \end{smallmatrix}$, crystallises from dilute alcohol in thick, yellow needles, melts at 225° , and is insoluble in water or organic solvents, except alcohol and acetic acid.

C. H. D.

Transformation of Trimethylgallic Acid and Trimethylpyrogallolcarboxylic Acid into Derivatives of Pyrogallol Trimethyl Ether, Antiarol, and Hexamethoxydiphenyl. CARL GRAEBE and MORITZ SUTER (*Annalen*, 1905, 340, 222—231).—Trimethylgallamide, $\text{OMe}\cdot\text{C} \begin{smallmatrix} \text{C(OMe)}\cdot\text{CH} \\ \diagup \text{C(OMe)}\cdot\text{CH} \end{smallmatrix} \text{C}\cdot\text{CO}\cdot\text{NH}_2$, is prepared by converting trimethylgallic acid into the acid chloride by treatment with phosphorus pentachloride in benzene solution and then passing in ammonia. When acted on by an alkaline solution of sodium hypochlorite, 5-aminotrimethylpyrogallol, $\text{OMe}\cdot\text{C} \begin{smallmatrix} \text{C(OMe)}\cdot\text{CH} \\ \diagup \text{C(OMe)}\cdot\text{CH} \end{smallmatrix} \text{C}\cdot\text{NH}_2$, is obtained, melting at $113\text{--}114^\circ$; its *acetyl* derivative crystallises in needles melting at 124° . When the base is diazotised and the solution boiled, the 1 : 2 : 3-trimethyl ether of 1 : 2 : 3 : 5-tetrahydroxybenzene is obtained; it forms colourless crystals melting at 146° , and is identical with Kiliani's antiarol.

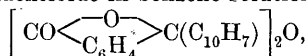
The trimethyl ether of pyrogallolcarboxylamide, prepared similarly to the gallamide, melts at $130\text{--}131^\circ$. From it 4-aminopyrogallol trimethyl ether, $\text{OMe}\cdot\text{C} \begin{smallmatrix} \text{C(OMe)}\cdot\text{C(OMe)} \\ \diagup \text{CH} \end{smallmatrix} \text{C}\cdot\text{NH}_2$, is prepared; it is an oil, and yields a hydrochloride melting at 181° . 4-Chloropyrogallol trimethylether, $\text{C}_9\text{H}_{11}\text{O}_3\text{Cl}$, is an oil and is prepared from 4-chloropyrogallol. 4-Iodopyrogallol trimethyl ether forms brownish-yellow crystals melting at $40\text{--}41^\circ$. 5-Chloropyrogallol trimethyl ether, prepared by diazotising the corresponding amino-derivative, forms crystals melting at 72° ; the analogous 5-iodo-derivative crystallises in yellow plates melting at $82\text{--}83^\circ$.

3 : 4 : 5 : 3' : 4' : 5'-Hexamethoxydiphenyl, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{C}_6\text{H}_2(\text{OMe})_3$, is prepared by heating 5-iodopyrogallol trimethyl ether with copper at 270° and forms crystals melting at 126° ; it can also be prepared from

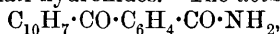
hydrocedrret and methyl sulphate. 2:3:4:2':3':4'-Hexamethoxydiphenyl is prepared from the 4-iodo-derivative and melts at 123°; it is also obtained from ellagic acid by melting with potassium hydroxide and treatment of the resulting product with methyl sulphate.

K. J. P. O.

Naphthoylbenzoic Acid. CARL GRAEBE (*Annalen*, 1905, **340**, 249—259).—1-Naphthoyl-2'-benzoic acid is best prepared by slowly adding aluminium chloride to a warm solution of naphthalene and phthalic anhydride in carbon disulphide. The *methyl* ester melts at 120°, and the *ethyl* ester at 123—124°. When the acid is warmed with phosphorus pentachloride in benzene solution, an *anhydride*,

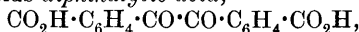


is produced, which forms crystals melting at 217°, and is only very slowly attacked by alkali hydroxides. The *acid amide*,



prepared by leading ammonia into a benzene solution of the acid containing phosphorus pentachloride, crystallises in colourless needles and melts at 215°.

When oxidised with an alkaline solution of permanganate, naphthoylbenzoic acid yields *diphthalic acid*,

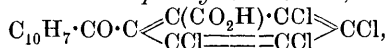


which forms crystals melting at 270°. If naphthylbenzoic acid is heated with an excess of phosphorus pentachloride at 220°, naphth-anthraquinone is formed quantitatively; the quinone is also obtained by oxidation of naphthanthracene, and can be oxidised to diphthalic acid.

K. J. P. O.

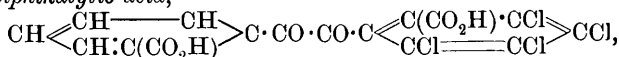
Tetrachloro- and Dichloro-naphthoylbenzoic Acids. CARL GRAEBE and WALTER PETER (*Annalen*, 1905, **340**, 259—266).—In order to prepare 1:2-naphthalenedicarboxylic acid, the chloronaphthoylbenzoic acids have been obtained, from which tetrachloronaphth-anthraquinone might be prepared and thence the dibasic acid. The attempt was, however, unsuccessful.

3:4:5:6-Tetrachloro-2-*naphthoylbenzoic acid*,



prepared by the action of aluminium chloride on a solution of naphthalene and tetrachlorophthalic anhydride in carbon disulphide, forms yellow crystals melting at 229°; the *sodium* salt crystallises with 4H₂O. The *methyl* ester is readily prepared by direct esterification at the ordinary temperature and thus forms an exception to Victor Meyer's rule; it forms crystals melting at 130°. When the acid is treated with concentrated sulphuric acid, tetrachloronaphthanthraquinone is not obtained, but a *sulphonic acid*, C₁₈H₈O₅Cl₄S, is formed. When heated with phosphorus pentachloride, tetrachloro-2-*naphthoylbenzoic acid* yields a *chloride*, C₁₈H₇O₂Cl₅, which forms crystals

melting at 214°. On oxidation with alkaline permanganate a *tetra-chlorodiphthalic acid*,



is obtained as crystals melting at 290°.

3:6-Dichloro-2-*a*-naphthoylbenzoic acid, $\text{C}_{10}\text{H}_7 \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{H}$, prepared by adding aluminium chloride to a solution of naphthalene and 3:6-dichlorophthalic anhydride in carbon disulphide, melts at 207·5°, and is converted into *a*-naphthoic acid by fusing with sodium hydroxide at 290°; the *methyl* ester forms crystals melting at 144°. When the acid is oxidised by permanganate, 3:6-dichlorodiphthalic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO}_2\text{H}$, is formed, melting at 216°. Sulphuric acid converts the dichloro-*a*-naphthoylbenzoic acid into dichloronaphthanthraquinonesulphonic acid, $\text{C}_6\text{H}_2\text{Cl}_2 \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \text{C}_{10}\text{H}_5 \cdot \text{SO}_3\text{H}$.

K. J. P. O.

Compounds of β -Phenylhydroxylamine with Aromatic Aldehydes. GIUSEPPE PLANCHER and GALEAZZO PICCININI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 36—43).— β -Phenylhydroxylamine serves as a general reagent for aldehydes, with which it forms the corresponding phenylaldoximes of the formula $\begin{array}{c} \text{CHR} \\ | \\ \text{NPh} \end{array} > \text{O}$. The following compounds have been prepared in this way.

Phenylbenzaldoxime, already obtained by Bamberger (*Abstr.*, 1894, i, 412) and by Gattermann (*Abstr.*, 1897, i, 189).

Phenylsalicylaldoxime, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{CH} \\ | \\ \text{NPh} \end{array} > \text{O}$, separates from alcohol as a yellow, crystalline powder melting at 118°, and dissolves slightly in light petroleum and readily in benzene.

Phenylanisalaldoxime, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{CH} \\ | \\ \text{NPh} \end{array} > \text{O}$, crystallises from alcohol in white needles melting at 118—119° and dissolves slightly in ether or light petroleum and readily in benzene.

Phenylhomosalicylaldoxime, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \begin{array}{c} \text{CH} \\ | \\ \text{NPh} \end{array} > \text{O}$, crystallises from alcohol in golden-yellow leaflets melting at 160°.

Phenylvanillaldoxime, already prepared electrolytically by the Farbenfabriken vorm. Friedr. Bayer (D.R.-P. 96564).

Phenylpiperonalaldoxime, $\text{CH}_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}_6\text{H}_3 \cdot \begin{array}{c} \text{CH} \\ | \\ \text{NPh} \end{array} > \text{O}$, crystallises from alcohol or from a mixture of benzene and light petroleum in radiating masses of colourless needles melting at 135°.

Phenyl-m-nitrobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \begin{array}{c} \text{CH} \\ | \\ \text{NPh} \end{array} > \text{O}$, crystallises from alcohol in pale yellow, silky needles melting at 151°, and dissolves slightly in ether, light petroleum, or benzene.

Phenylcinnamaldoxime, $\text{CHPh} \cdot \text{CH} \cdot \underset{\text{NPh}}{\text{CH}} > \text{O}$, separates from alcohol in minute, yellow crystals melting at $150-151^\circ$.

Phenylcuminaldoxime, $\text{CHMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \underset{\text{NPh}}{\text{CH}} > \text{O}$, separates from alcohol in straw-yellow, prismatic crystals melting at $96-97^\circ$, and is soluble in benzene.

p-Tolyl-m-nitrobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \underset{\text{C}_6\text{H}_4\text{Me}}{\text{CH}} > \text{O}$, crystallises from alcohol in shining scales melting at 161° , and is slightly soluble in light petroleum or ether, and more so in benzene.

It is noteworthy that such of the above compounds as contain a free hydroxyl group have a yellow colour. T. H. P.

Secondary Reaction of Magnesium Alkyl Haloids. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1905, 141, 298—301. Compare Abstr., 1904, i, 666, 809).—When *cyclohexanone* reacts with magnesium *isobutyl* bromide, not more than 10 per cent. of the theoretical yield of *tert.-isobutylcyclohexanol* is obtained. During this reaction, butylene is evolved, and the crystalline product $\text{C}_6\text{H}_{11}\text{O} \cdot \text{MgI}$ is formed, which in contact with water furnishes *cyclohexanol*. Secondary reactions of this type occur as a rule only to a slight extent when the Grignard reaction is applied to aliphatic or aromatic aldehydes, chloral being the most notable exception. With ketones, and especially cyclic ketones, on the contrary, the secondary reaction assumes greater importance. The nature of the alkyl group in the magnesium alkyl haloid used also exerts some influence on the extent to which the secondary reaction takes place; thus *isobutyl* favours its occurrence, whilst primary aliphatic alkyl groups as a rule show this tendency to a much less extent, and aromatic alkyl groups do not exhibit it at all. Magnesium haloid derivatives of *sec.*-alkyl groups always furnish the secondary reaction to a greater or less extent. A number of cases illustrating these observations are quoted.

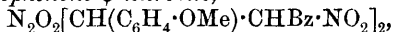
T. A. H.

ψ -Nitrosites of Unsaturated Ketones. HEINRICH WIELAND and SIEGFRIED BLOCH (*Annalen*, 1905, 340, 63—85. Compare Abstr., 1904, i, 54, 415, 596).—The addition of N_2O_4 to the ethylene linking of phenylethylenes, $\text{CHPh} \cdot \text{CHR}$, takes place in two ways according as the group R is of positive or of negative character: if R is positive, bimolecular ψ -nitrosites are formed, but if R is negative, as in unsaturated ketones or aldehydes, saturated unimolecular compounds are produced. The presence of positive substituents in the benzene nucleus neutralises the effect of the negative character of R; thus, for example, whilst benzylideneacetone or benzylideneacetophenone do not give nitrosites, the corresponding anisylidene compound yields such a derivative.

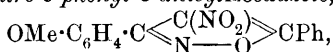
The ψ -nitrosites break up, when boiled with alcohol, into the unimolecular nitro-oximes, $\cdot\text{C}(\text{NOH}) \cdot \text{CH}(\text{NO}_2) \cdot$, which then lose water,

forming glyoximeperoxides, $\cdot\overset{\cdot}{\underset{|}{\text{C}}}\text{---}\overset{\cdot}{\underset{|}{\text{C}}}\cdot$
 $\text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N}$, if positive groups are present
 in the benzene nucleus. The nitro-oximes can also lose water in
 another manner from the corresponding enol, $\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NO}_2)\cdot\text{C}(\text{OH})\cdot$,
 yielding β -nitroisooxazoles, $\cdot\text{C}\langle\overset{\text{C}(\text{NO}_2)}{\text{N}\text{---}\text{O}}\rangle\text{C}\cdot$. The anisylideneacetone
 ψ -nitrosites yield nitro-oximes which lose water, forming pyrrole
 derivatives, the methyl group sharing in the condensation, thus:
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{CH}(\text{NO}_2)\cdot\text{CO}\cdot\text{CH}_3 \rightarrow$
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\underset{\text{NH-CH}_2}{\underset{|}{\text{C}}}\cdot\text{C}(\text{NO}_2)\rangle\text{CO}.$

Anisylideneacetophenone ψ -nitrosite,



prepared by passing nitrous fumes into an alcoholic solution of
 anisylideneacetophenone in absolute alcohol cooled to 0° , crystallises in
 yellow needles melting and decomposing at 112° , and gives with
 sulphuric acid an intense red coloration. Boiling with alcohol
 converts it into 4-nitro-5-phenyl-3-anisylisooxazole,



which crystallises in needles and dissolves in alcoholic potassium
 hydroxide. When reduced with zinc dust and acetic acid in the pre-
 sence of methyl alcohol, 4-amino-5-phenyl-3-anisylisooxazole, $\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$,
 is obtained as crystals melting at 123° ; its hydrochloride melts at 185° .
 The nitronitrite, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{O}\cdot\text{NO})\cdot\text{CH}(\text{NO}_2)\cdot\text{COPh}$, is formed at
 the same time as the ψ -nitrosite, and is obtained by evaporating the
 ethereal mother-liquor; it is decomposed by ammonia into anisaldehyde
 and nitroacetophenone, and when shaken with dilute sodium hydroxide
 into anisylidene- α -nitroacetophenone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{NO}_2)\cdot\text{COPh}$, a
 viscid, yellow oil which decomposes explosively when heated in a
 vacuum at 115° .

Anisylideneacetone ψ -nitrosite, $\text{C}_{22}\text{H}_{24}\text{O}_{10}\text{N}_4$, is a white, crystalline
 powder decomposing at 111° , and when boiled with alcohol is converted
 into 4-nitro-5-anisyl-3-pyrrolone; the latter crystallises in golden-yellow
 needles melting at 89° , and gives an olive-green coloration with
 sulphuric acid. On reduction with stannous chloride and hydrochloric
 acid, 4-amino-5-anisyl-3-pyrrolone hydrochloride, $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$, is
 obtained in needles melting at 214° ; the base forms crystals melting at
 97° . α -Nitroanisylideneacetone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{NO}_2)\cdot\text{COPh}$, is obtained
 by allowing the ethereal mother-liquor, from which the ψ -nitrosite has
 separated, to remain in contact with water; it crystallises in four-sided
 prisms melting at 124° , and with sulphuric acid gives an orange
 coloration which passes into violet; dilute sodium hydroxide converts
 it into β -nitro- α -anisylethylene (m. p. 87°), and alcoholic ammonia gives
 rise to nitroacetone.

K. J. P. O.

**Condensation of Naphthalaldehydic Acid with *m*-Tolyl
 Methyl Ketone, Pinacolone, and Acenaphthenone.** SIEGFRIED
 WIECHOWSKI (*Monatsh.*, 1905, 26, 749—763. Compare Zink, *Abstr.*,
 1902, i, 34, 159; Goldschmiedt and Krezmař, *Abstr.*, 1902, i, 41;

Luksch, this vol., i, 68).—*m*-Tolyl naphthalidomethyl ketone, formed by warming naphthalaldehydic acid with *m*-tolyl methyl ketone in dilute sodium hydroxide solution at 38° for 48—72 hours, is precipitated on addition of hydrochloric acid to the reaction mixture in large, yellow, oily drops which change into the colourless, crystalline *pseudo*-acid, $\text{CO} \langle \text{C}_{10}\text{H}_6 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_7\text{H}_7$. This melts at 118—120°, is easily soluble in hot alcohol, hot glacial acetic acid, benzene, or chloroform, but only slightly so in ether, and dissolves in aqueous potassium hydroxide or sodium carbonate to form yellow solutions which decompose on boiling, giving an odour of *m*-tolyl methyl ketone.

The *oxime*, $\text{CO} \langle \text{C}_{10}\text{H}_6 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{C}_7\text{H}_7) \cdot \text{N} \cdot \text{OH}$, formed by the action of hydroxylamine hydrochloride on the *pseudo*-acid in alcoholic solution, crystallises in colourless, probably monoclinic crystals, melts at 163°, has a neutral reaction to litmus, is insoluble in cold, but is decomposed by warm, aqueous alkali hydroxides, and is decomposed into hydroxylamine and the *pseudo*-acid when boiled with hydrochloric acid. The action of hydroxylamine and aqueous sodium hydroxide on naphthalidomethyl *m*-tolyl ketone in alcoholic solution leads to the formation of two products: (a) a small quantity of a substance which crystallises from glacial acetic acid, melts and decomposes at 235°, and contains nitrogen, and (b) a yellow, crystalline, sodium salt of the *oxime* or of the oxamino-*oxime* anhydride of *m*-tolyl naphthalidomethyl ketone.

The phenylhydrazone, $\text{C}_{27}\text{H}_{22}\text{O}_2\text{N}_2$, separates from glacial acetic acid in small, yellow crystals, melts at 152—155°, is insoluble in aqueous alkali hydroxides, is decomposed with formation of phenylhydrazine by concentrated or by hot alcoholic hydrochloric acid, and dissolves in concentrated sulphuric acid to a red solution which darkens on addition of potassium dichromate.

m-Tolacylnaphthalimidine, $\text{CO} \langle \text{C}_{10}\text{H}_6 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_7\text{H}_7$, formed by shaking *m*-tolyl naphthalidomethyl ketone with saturated aqueous ammonia, forms slender, white needles, melts at 152—154°, and when heated with hydrochloric acid, or more rapidly but with partial decomposition when heated with aqueous potassium hydroxide, is converted into a yellow *isomeride* which melts and partially decomposes at 234°, and is decomposed by boiling aqueous potassium hydroxide or hydrochloric acid.

Naphthalidopinacolin, $\text{CO} \langle \text{C}_{10}\text{H}_6 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CMe}_3$, formed by the condensation of naphthalaldehydic acid with pinacolin in dilute sodium hydroxide solution, separates from alcohol in heavy crystals, melts at 113—114°, and is decomposed by boiling aqueous alkali hydroxides. The *oxime*, $\text{CO} \langle \text{C}_{10}\text{H}_6 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{NOH}) \cdot \text{CMe}_3$, formed by the action of hydroxylamine hydrochloride on naphthalidopinacolin in alcoholic solution, melts at 187—189° and is insoluble in aqueous alkali hydroxides. No imidine could be obtained by treating naphthalidopinacolin with ammonia.

The *condensation product* of naphthalaldehydic acid with acenaphthenone, $\text{C}_{10}\text{H}_6 \cdot \text{C}(\text{H}) \cdot \text{CH}(\text{CO}) > \text{C}_{10}\text{H}_6$, forms transparent crystals, melts at 226—227°, and remains unchanged when shaken with saturated aqueous ammonia. G. Y.

[**Methoxy-derivatives of Anthraquinone.**] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158257).—A solution of bromine in glacial acetic acid converts alizarin 2-methyl ether into 4-bromoalizarin 2-methyl ether, which crystallises from acetic acid in orange needles, melts at 234—235°, and dissolves sparingly in alcohol, more readily in benzene. It is insoluble in sodium carbonate, but dissolves in sodium hydroxide to a red solution, which deposits the sodium salt on cooling.

When boiled with *p*-toluidine, 4-*p*-toluidinoalizarin 2-methyl ether, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}(\text{OMe})(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, is formed, and crystallises in glistening, violet needles, soluble in alcohol to a reddish-violet solution, and in concentrated sulphuric acid to a blue solution. A similar compound is obtained from aniline. On sulphonating at the ordinary temperature with fuming sulphuric acid, red or violet dyes are obtained, yielding green shades with chromium salts. C. H. D.

Preparation of Camphor. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 158717).—Whilst bornyl acetate only yields 10 per cent. of camphor on oxidation (Schrötter, Abstr., 1882, 66), isobornyl acetate yields as much as 90 per cent. of camphor on oxidation with chromic acid, nitric acid, potassium permanganate, or Caro's acid. The isobornyl acetate obtained in the preparation of isoborneol from camphene may be employed without saponification. Less favourable results are obtained with the formate or benzoate.

C. H. D.

Terpenes and Ethereal Oils. OTTO WALLACH (*Annalen*, 1905, 340, 1—16. Compare Abstr., 1903, i, 103, 105, 576; 1904, i, 1035).—The nitrite of β -phellandrene is best prepared by the action of nitrous acid on a solution of phellandrene in light petroleum; the small yield (25 per cent.) is due to the fact that part of the hydrocarbon escapes the action of the nitrous acid and that part of the nitrite is oxidised to nitrophellandrene and other compounds. Pure phellandrene nitrite is completely, although slowly, soluble in 10 per cent. sodium hydroxide.

On reducing nitrophellandrene in acetic acid by zinc dust or in alcohol by sodium, compounds are obtained which are partly of basic character and partly substances containing oxygen; they belong to the hydroaromatic group. Dihydrocuminaldehyde, $\text{C}_{10}\text{H}_{14}\text{O}$, was obtained by reduction with zinc dust and acetic acid after removal of the basic products; it is an oil boiling at 111—112° under 13 mm. pressure; its semicarbazone crystallises in needles melting at 200—202°. When oxidised by sodium hypobromite, cumic acid is formed, whilst silver oxide gives as well dihydrocumatic acid, $\text{C}_{10}\text{H}_{14}\text{O}_2$, which melts above 130°. With sodium and alcohol as the reducing agent, cuminaldehyde,

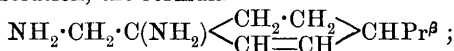
and not dihydrocumininaldehyde, is produced together with other substances; it was recognised in the form of its aldoxime (m. p. 58—59°)

The basic products of reduction, which are easily separated as hydrochlorides, consist of a mixture of hydrocuminylamine (di- or tetra-hydrocuminylamine) with cuminyllamine. The *hydrocuminylamine* is identical with Pesci's aminophellandrene, and is readily isolated as its *carbamide*, which is but sparingly soluble and crystallises in broad lamellæ melting at 160—161°, and has $[\alpha]_D +58.566^\circ$ in alcoholic solution.

These results show that β -phellandrene has a methylene group as a side-chain with an *isopropyl* group in the para-position; further, from the molecular refraction it follows that two ethylene linkings are present, and from the optical activity an asymmetric carbon atom.

The formula $\text{CH}_2:\text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}=\text{CH} \end{smallmatrix} \text{CHPr}^\beta$ expresses these facts; the

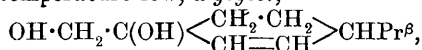
nitrite then has the formula $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{NO}) \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}=\text{CH} \end{smallmatrix} \text{CHPr}^\beta$, and the β -phellandrenediamine, obtained by careful reduction of the nitrite in acid solution, the formula



either the formula $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CH}=\text{CH} \end{smallmatrix} \text{CHPr}^\beta$ or the formula

$\text{NO}_2 \cdot \text{CH}:\text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}=\text{CH} \end{smallmatrix} \text{CHPr}^\beta$ must then be ascribed to nitrophellandrene.

*iso*Butyric acid is the final product when phellandrene is oxidised with excess of permanganate. When the hydrocarbon is kept in large excess and the temperature low, a *glycol*,



is formed together with a considerable quantity of volatile and non-volatile acids; the glycol is a colourless liquid boiling at 150° under 10 mm. pressure, and when treated with dilute sulphuric acid is converted into a *tetrahydrocumininaldehyde*, $\text{CHPr}^\beta \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}=\text{CH} \end{smallmatrix} \text{CH} \cdot \text{CHO}$,

which is a liquid boiling between 220° and 230°, and having a sp. gr. 0.93 at 20° and n_D 1.4903 at 20°. The *semicarbazone* crystallises in needles melting at 204—205°, and the *oxime* in six-sided plates melting at 87°. When oxidised with silver oxide, the aldehyde yields *tetrahydrocuminic acid*, $\text{C}_{10}\text{H}_{16}\text{O}_2$, which melts at 143—144°. K. J. P. O.

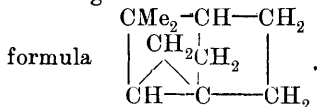
Camphene. STEFAN MOYCHO and FRANZ ZIENKOWSKI (*Annalen*, 1905, 340, 17—63. Compare Abstr., 1904, i, 438).—Since the

evidence for Wagner's formula for camphene, $\begin{array}{c} \text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 : \text{C} \text{---} \text{CH} \cdot \text{CH}_2 \end{array}$, is indirect, an attempt has been made to obtain more certain proof.

From the oxidation products of camphene (*loc. cit.*), two additional acids have been isolated, the sodium salts of which are but sparingly

soluble. One acid, $C_{10}H_{14}O_3$, melts at 139.5° and the other, which has not been investigated fully, at 90° . On dry distillation of a liquid mixture of these acids, a lactone, $C_9H_{14}O_3$, is obtained crystallising in monoclinic plates and melting at $95-96^\circ$.

The cyclene (*loc. cit.*), which is converted into bornyl acetate by warming with acetic acid and sulphuric acid, is best represented by the



Camphene glycol, which when pure melts at 200° , yields on esterification with benzoyl chloride in pyridine solution a *monobenzoate*, $C_{10}H_{17}O_2Bz$, which crystallises in prisms melting at 88° , and is reconverted into the glycol on hydrolysis. On treatment with phosphorus pentachloride or hydrogen chloride in chloroform solution, the monobenzoate is converted into an unsaturated *monobenzoate*, $C_{10}H_{15}OBz$, which melts at $85-86^\circ$, and on hydrolysis with alcoholic potassium hydroxide yields camphenilaldehyde, and on oxidation with potassium permanganate camphenilone. These facts are in favour of Wagner's formula for camphene in that the group $:C:CH_2$ is present, whilst they are opposed to Bredt's view of the changes of camphene. The transformations from camphene through the glycol to the aldehyde are represented thus: $C_8H_{14}:C:CH_2 \rightarrow C_8H_{14}:C(OH)\cdot CH_2\cdot OH \rightarrow C_8H_{14}:C(OH)\cdot CH_2\cdot OBz \rightarrow C_8H_{14}:C:CH\cdot OBz \rightarrow C_8H_{14}:C:CH\cdot OH \rightarrow C_8H_{14}:CH\cdot CHO$. All these observations are in favour of the view that the hydration product of camphene is a true glycol.

When the pure glycol is oxidised by permanganate in 4 per cent. aqueous solution, besides camphenilone and camphenilic acid, a new acid, $C_{10}H_{14}O_3$, is obtained crystallising in prisms melting at 139° . The relation of this acid to camphenilic acid has not yet been demonstrated; it is possible that the erroneous statement that camphenecamphoric acid is obtained in the oxidation of camphene is due to the new acid being mistaken for camphenecamphoric acid; the melting points lie near together.

A consideration of numerous observations, recorded both in this paper and previously, lead to the conclusion that the camphene obtained from *isoborneol* consists of a mixture of three hydrocarbons: (i) camphene, the oxidation products of which are camphene glycol, and then camphenilic acid and camphenilone; (ii) camphene from which camphenecamphoric acid can be obtained, and (iii) the saturated cyclene, of which the oxidation products have not yet been investigated. The first of these three hydrocarbons alone contains the group $:C:CH_2$.

The neutral oxidation product of camphene, $C_{10}H_{16}O_2$ (*loc. cit.*), which melts at $169-170^\circ$, with benzoyl chloride in pyridine solution yields a *monobenzoate* melting at 71° , which, however, is not attacked by phosphorus pentachloride; the substance only contains one hydroxyl group, and must, therefore, be a hydroxyoxide. It is not probable that the hydroxyoxide is formed from camphene glycol, since neither the oxide nor its oxidation product, the acid $C_{10}H_{14}O_3$, melting at $198-200^\circ$, can be found among the oxidation products of the glycol.

It is worthy of note that the acid $C_{10}H_{14}O_3$ (m. p. 138.5°), obtained from the glycol, can be changed into the isomeric acid from the hydroxyoxide. It is suggested that the hydroxyoxide is formed from cyclene.

The acid $C_{10}H_{14}O_3$ (m. p. 138.5°), which is formed, together with camphenilic acid and an acid melting at about 90° , in the oxidation of camphene, is isolated in the form of a sparingly soluble *sodium* salt, and crystallises in large, four-sided prisms. The acid reacts with one mol. of phosphorus pentachloride, and not at all with semicarbazide; one atom of oxygen must, therefore, be present as oxide. It forms an additive product with hydrogen chloride, $C_{10}H_{15}O_3Cl$, which contains a hydroxyl group and reacts with benzoyl chloride in the presence of pyridine, yielding a *benzoate* melting at 110° . The additive product is reconverted into the original acid by treatment with alcoholic potassium hydroxide, but if first heated with silver acetate and then hydrolysed, an isomeric acid (m. p. $198-200^\circ$) is obtained which is identical with the product of oxidation of the hydroxyoxide mentioned in the foregoing paragraph.

$$\begin{array}{c} CMe_2-CH\cdot CO_2H \\ | \\ CH_2 \\ | \\ CHMe\cdot CH\cdot CO_2H \end{array}$$

Camphenecamphoric acid, (?), is the main oxida-

tion product of the camphene obtained from *isoborneol*, and is formed from the neutral oxidation product remaining after campheneglycol and the hydroxyoxide have been removed. This neutral substance on keeping gradually changes into the acid. The acid yields a *diamide*, $C_{10}H_{18}O_2N_2$, crystallising in scales melting at 222° , from which the *carbamate*, $C_8H_{14}(NH\cdot CO_2Me)_2$, crystallising in plates melting at 114° , can be prepared by the action of bromine and sodium methoxide. The *dianilide* crystallises in needles melting at 210° . The *dinitrile*, prepared by dry distillation of the diamide, is a liquid boiling at $173-175^\circ$ under 14 mm. pressure, and when reduced with sodium and alcohol yields *camphenecamphoryldiamine*, $C_8H_{14}(CH_2\cdot NH_2)_2$.

Camphenilic acid can be acylated when the ester is treated with acyl chlorides in the presence of pyridine. The *acetyl* derivative is a liquid boiling at $138.5-139.5^\circ$ under 12 mm. pressure, and the *benzoyl* derivative a solid melting at 168° . When heated above its melting point, the acid decomposes into carbon dioxide, water, and a hydrocarbon, C_9H_{14} , which boils at $137.5-138.5^\circ$ and is possibly identical with Jagelki's camphenylene.

When camphenilone is treated with sodium and amyl formate in order to prepare a hydroxymethylene derivative, the *pinacone*, $C_{18}H_{30}O_2$, is formed, two modifications melting at $173-173.5^\circ$ and at $172.5-173^\circ$ respectively being obtained; camphenilone does not contain a carbonyl group attached to a methylene group. The ketone cannot be readily oxidised, but is converted by phosphorus pentachloride into a *dichloride*, $C_9H_{14}Cl_2$, which forms soft crystals melting at 174° . Treatment with sodium decomposes this chloride, apobornylene (m. p. 34° , and b. p. $136-137^\circ$) and other substances being produced.

The alcohol, methylcamphenilol, prepared from camphenilone (*loc.*

cit.), is a structural isomeride of *isoborneol*, since the two alcohols behave differently on oxidation with chromic acid. K. J. P. O.

Essential Oils from Liverworts. KARL MÜLLER (*Zeit. physiol. Chem.*, 1905, **45**, 299—319).—All liverworts appear to contain essential oils. From *Mastigobryum trilobatum*, an oil distilling at 260—265° was obtained. It has the composition $C_{10}H_{16}$, sp. gr. 0.946 at 20°, and $[\alpha]_D + 25.95^\circ$, and on oxidation yields a ketone, $C_{10}H_{16}O$. A fraction boiling at 270—285° with $[\alpha]_D + 42.21^\circ$ and sp. gr. 0.820 was also obtained. *Leioscyphus Taylora* yields a considerable amount of a green oil with a high sp. gr. and large saponification value, and probably contains two alcohols, $C_{15}H_{26}O$, and a terpene or sesquiterpene. *Madotheca levigata* yields an oil of low sp. gr. and rich in readily volatile compounds. The fraction boiling at 280° is characterised by its high rotation ($+132^\circ$) and seems to contain about 10 per cent. of an alcohol, $C_{10}H_{18}O$. *Alicularia scalaris* yields a small amount of a levorotatory yellow oil. J. J. S.

Balata. ALEXANDER TSCHIRCH and E. SCHERESCHEWSKI (*Arch. Pharm.*, 1905, **243**, 358—377).—Balata, or “Surinam gutta-percha,” the most important substitute for gutta-percha, is the product of *Mimusops globosa* (or *M. Balata*), one of the *Sapotaceæ*, which grows in Guiana. Of the sample examined, water dissolved 5.7, alcohol 41.5 (resin), acetone 42.5, ether 87, and chloroform 87 (resin + gutta) per cent. The loss at 100° in several hours (moisture) was 1.72, ash 0.96, and impurities 10.5 per cent.

No substances volatile with steam were present. Water extracted a *gum* insoluble in alcohol, mixed with *proteid* material, from which it was freed by means of tannic acid; it amounted then to 1.5 per cent. of the drug. The gum was optically inactive, even after boiling with acid, and was not fermented by yeast; it reduced Fehling's solution and gave the α -naphthol-sulphuric acid reaction; when it was charred or boiled with dilute sulphuric acid, the vapours evolved gave the reaction for furfuraldehyde, and when it was fused with potassium hydroxide the vapour gave the reaction of pyrrole; it gave 6.5 per cent. ash. No oxydase was present.

The material was then extracted with boiling alcohol, which dissolved the *resin*. As the solution cooled a substance separated, which was further separated by treatment with alcohol at 50° into the readily soluble β -*balalban*, $C_{27}H_{44}O_2$ or $C_{27}H_{46}O_2$ (molecular weight determined), which crystallises in lustrous scales and melts at 108—109°, and the sparingly soluble α -*balalban*, $C_{27}H_{42}O_2$, which crystallises in needles and melts at 230—231°. The former was obtained in much larger amount; when boiled with alcoholic potassium hydroxide, it yielded a small quantity of a *substance* which melted at 116—117° and contained C 82.9, H 12.3 per cent. No cinnamic ester is present in the drug; neither is it, however, in all samples of gutta-percha. When the alcoholic liquid from which the alban had separated was poured into very dilute hydrochloric acid, *balafuavil*, $C_{10}H_{18}O$, was precipitated in amount equal to about 1.5 per cent. of the drug; it is a sticky, amorphous substance.

The residual material was next dissolved in chloroform, the solution diluted with half its volume of ether, and alcohol added until a permanent turbidity resulted; *balagutta*, $C_{10}H_{18}$, separated gradually in needles curved like sickles or commas; it is very unstable in the presence of air, although the drug which contains it is stable. By adding much alcohol to the mother liquor, *balalbanan* was precipitated; it was crystallised from a mixture of alcohol and ether, when it melted at $55-56^{\circ}$ and contained C 77.7—82.3, H 11.9—12.2 per cent.; it oxidises very readily in the air. C. F. B.

Gentiin. GEORGES TANRET (*Compt. rend.*, 1905, 141, 263—264).—*Gentiin*, $C_{25}H_{28}O_{14}$, occurs in the mother liquors resulting from the purification of gentiopiecin (this vol., i, 655). It separates from boiling alcohol in microscopic, slightly yellow needles, melts and decomposes at 274° , and gives a green coloration with nitric acid and greenish-black with ferric chloride. Gentiin is slowly hydrolysed by dilute sulphuric acid at 100° , forming dextrose (1 mol.), xylose (1 mol.), and *gentienin*, $C_{14}H_{10}O_5$ (1 mol.). The last-mentioned substance crystallises from boiling alcohol in sulphur-yellow needles, begins to sublime at 195° , and melts at 225° . It is isomeric with gentisin, but melts at a lower temperature and gives a yellow in place of a green coloration with nitric acid. It is stated that gentiin is the first recorded glucoside yielding xylose as a product of hydrolysis. T. A. H.

Process of Dyeing Animal Textile Fibres. P. GELMO and WILHELM SUIDA (*Monatsh.*, 1905, 26, 855—878. Compare Suida, this vol., i, 457; Knecht, Abstr., 1889, 49).—The affinity of wool which has been treated with very dilute aqueous or alcoholic sulphuric acid and washed with hot water is diminished towards basic but increased towards acid dyes, but the affinity towards acid dyes is diminished if the treatment and washing are carried out at the laboratory temperature. The action of hydrochloric acid on wool is similar to that of sulphuric acid; the behaviour towards dyes of wool which has been treated with dilute acetic acid and thoroughly washed is the same as that of untreated wool, but the affinity towards basic dyes is diminished if the dyeing takes place immediately after the treatment with acetic acid and without washing. The effect of tartaric acid on wool is intermediate between that of sulphuric acid and that of acetic acid.

When boiled with water or an aqueous solution of aluminium sulphate or of sulphuric acid, wool undergoes such a considerable loss in weight, owing to the formation of soluble amino-acids, that quantitative mordanting experiments cannot be carried out. Wool and silk were boiled with $N/10$ ammonia, hydrochloric acid, and sulphuric acid, and the reagent remaining unabsorbed titrated, using methyl-orange as indicator; the reaction was complete in five minutes. Two specimens of wool and one of silk were found to absorb ammonia, hydrochloric acid, and sulphuric acid in the respective proportions: $NH_3 : 2HCl : 2.4H_2SO_4/2$; $NH_3 : 2HCl : 2.1H_2SO_4/2$; and $6.4NH_3 : HCl : 2H_2SO_4/2$ (compare Mills and Takamine, *Trans.*, 1883, 43, 142). The difference in behaviour of the two specimens of wool agrees with the fact that some wools are alkaline,

whilst others are neutral to phenolphthalein. The dyeing of purified wool by pure acid dyes set free from their salts by means of fuming hydrochloric acid, washed and dried, is not increased by the addition of mineral acids. Owing to its acid nature, wool forms salts when treated with aqueous alkali carbonates or with hard water, and it is to neutralise these that the mineral acid necessary in dyeing is required. When heated with alcoholic potassium hydroxide and washed with water, wool forms potassium compounds which give stronger colours with benzopurpurin 6B and with Bordeaux extra. This behaviour is not altered by steeping the treated wool in very dilute acetic acid.

Wool which has been heated on the water-bath with 0.1 per cent. alcoholic zinc chloride gives weaker colours with basic dyes, but a stronger colour with azomagenta G in a neutral bath, than when heated with aqueous zinc chloride. No difference could be observed in the behaviour towards alizarin-red S or anthracene-blue WG of wool mordanted with chromium sulphate with or without previous treatment with dilute sulphuric acid; but wool mordanted with aluminium sulphate after treatment gives stronger colours, whilst wool mordanted with ferric sulphate after treatment gives weaker colours, than does wool mordanted with these salts without previous treatment with sulphuric acid. Untreated wools mordanted with chromium, aluminium, or ferric sulphates behave towards basic and acid dyes in the same manner as does wool treated with sulphuric acid but not mordanted. This behaviour is reversed by treatment of the mordanted wool with aqueous ammonium carbonate. Wool which has been boiled with *N*/10 aluminium acetate or tartrate cannot be dyed with direct dyes, which points to neutralisation of the acid groups of the wool.

Wool is hydrolysed by boiling water, or more quickly by dilute mineral acids or solutions of mordanting salts; its soluble products of hydrolysis are therefore always formed during the process of dyeing. The reactions of these soluble products show the presence of a peptone, which, on further hydrolysis, must break down to simpler amino-acids. The aminobenzoic acids precipitate crystal-violet O and pararosaniline from neutral baths, as also azomagenta G from its solution in weak acetic acid, and assist therefore the process of dyeing, whilst the fatty amino-acids do not do so. The presence of peptone causes colours obtained on dyeing wool with basic dyes in neutral solutions not to be fast to soaping, whilst dyeing is not obtained with acid dyes in neutral solution, but in a weak acid bath acid dyes give fast colours.

Experiments show that whilst untreated wool is only moderately dyed, wool which has been heated with 0.5 per cent. aqueous or alcoholic sulphuric acid is intensely dyed by azomagenta G or crystal-ponceau, but only the dyed wool previously treated with alcoholic sulphuric acid is fast to soaping.

The hydrolysis of wool is necessary to the process of dyeing. It is possible that wool is an anhydro-compound, the active groups of which are formed only on hydrolysis. When treated with alcoholic sulphuric acid, wool apparently loses its acid characters, becoming basic and capable of uniting with mineral acids. The salts so formed undergo double decomposition with acid dyes, but cannot enter into reaction with basic dyes.

G. Y.

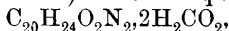
Homologues of Quinophthalone. ALEXANDER EIBNER (D.R.-P. 158761. Compare Abstr., 1904, i, 930, 931).—The mixture of quinophthalones and *isoquinophthalones*, obtained by the action of phthalic anhydride on quinaldine derivatives, may be converted into pure quinophthalones by warming on the water-bath with an alcoholic solution of sodium ethoxide. The sodium derivatives thus obtained are decomposed by boiling water and dried at 100°.

6:8-Dimethylquinophthalone, $C_9NH_4Me_2 \cdot CH:C_8H_4O_2$, forms a golden-yellow powder and melts at 290°. 5:6:8-Trimethylquinophthalone forms a dark golden-yellow powder and melts at 294°. β -Naphthaquinophthalone, $C_{13}NH_3 \cdot CH:C_8H_4O_2$, forms an orange powder and melts at 326°.

The dyeing power, fastness towards light, and insolubility in alcohol or chloroform increase with increase in the molecular weight.

C. H. D.

Quinine Formates. HUNKIARBÉYENDIAN LACROIX (*J. Pharm. Chim.*, 1905, [vi], 22, 99—103).—Normal quinine formate,



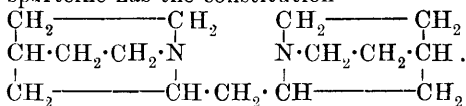
obtained by dissolving one part of quinine in two parts of formic acid, is an unstable salt which dissolves in water giving an acid solution; it crystallises in long, white, glistening needles which melt at 95° and lose formic acid below 50°. Basic quinine formate, $C_{20}H_{24}O_9N_2 \cdot H_2CO_2$, is prepared by adding the calculated amount of glacial formic acid to quinine suspended in water at 50°; it crystallises from the solution on cooling in tufts of white, silken needles melting at 132°; it contains more quinine than any other quinine salt; its aqueous solution, which is neutral to litmus and is not fluorescent, has $[\alpha]_D -141.1^\circ$ at 21°. A 2 per cent. solution at 21° has $n_D 1.336$. It dissolves in nineteen parts of water at 16° and in six parts at 42°.

P. H.

Sparteine. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1905, 141, 261—262 and 328—330. Compare this vol., i, 608—609, and Willstätter and Marx, *ibid.*, i, 544).—The products described in the first of these papers were obtained in the course of an investigation of the substances produced by the exhaustive methylation of sparteine. The alkylsparteines described are in each case mixtures of isomerides and are tertiary unsaturated bases, which readily reduce permanganate.

Methylsparteine, $N:C_{15}H_{25}NMe$, obtained by distilling methylsparteinium hydroxide, $N:C_{15}H_{26}NMe \cdot OH$ (sparteinemethylammonium hydroxide), prepared from sparteine α -methiodide by the action of silver hydroxide, may be separated into fractions boiling between 171° and 175° under 11.5 mm. pressure and having $[\alpha]_D$ ranging from -19.67° to -40.0° in alcohol. *Dimethylsparteine*, similarly prepared from sparteine dimethylammonium hydroxide, is an oil boiling at 182—193° under 13.6 mm. pressure. When sparteinetrimethylammonium hydroxide is heated at 200—210°, it decomposes, yielding trimethylamine and *hemisparteilene*, $C_{15}H_{23}N$, which boils at 135—155° under 13 mm. pressure.

Taking into consideration the facts already established with regard to the chemistry of sparteine (*loc. cit.*), and accepting the view of Willstätter and Marx that the alkaloid is not a tropane derivative (compare Wackernagel and Wolfenstein, *Abstr.*, 1904, i, 917), it is probable that sparteine has the constitution



The location of the linking methylene group is deduced from the fact that sparteine yields two stereoisomeric methiodides (this vol., i, 608), and must therefore have a constitution analogous to those of conhydrine and conicine (compare Scholtz, *Abstr.*, 1904, i, 1044).

T. A. H.

Alkaloids of some Solanaceæ which induce Mydriasis. ERNST SCHMIDT (*Arch. Pharm.*, 1905, 243, 303—309).—This paper for the most part is introductory to those of which accounts are given in the following abstract and this vol., ii, 648.

Datura Metel has been shown to contain scopolamine (hyoscyne) as almost the only constituent of alkaloidal nature; this may be of practical importance, as the plant is easily cultivated.

Datura arborea also contains scopolamine as the main alkaloid, but some hyoscyamine is also present.

Atropa belladonna contains hyoscyamine as almost the only alkaloid in all parts of the plant; the amount found was about 0·8 per cent. in the cultivated plant, 0·4 in that growing wild.

C. F. B.

Alkaloids from certain Species of *Datura* which induce Mydriasis. ADOLF KIRCHER (*Arch. Pharm.*, 1905, 243, 309—328).—The leaves of *Datura Metel* contain 0·55, the seeds 0·50 per cent. of alkaloids, reckoned as scopolamine, which forms the bulk of them; small quantities of hyoscyamine and atropine are present also.

The leaves of *Datura quercifolia* contain 0·42, the seeds 0·29 per cent. of alkaloids. In the leaves, stems, unripe fruits, and roots, scopolamine and hyoscyamine are present in about equal proportions; in the seeds, hyoscyamine greatly predominates.

All parts of *Datura arborea* (*D. suaveolens*, *Brugmansia candida*) contain scopolamine; a small amount of hyoscyamine was found also in the stem and root, of which alone a considerable quantity was available for examination.

Datura stramonium contains mainly hyoscyamine. Confirmation was obtained of Feldhaus' discovery (*Inaug. Diss.*, Marburg, 1903) that the percentage of alkaloid in the medial rib and stem of the leaf of the growing plant diminishes gradually after the rest of the leaf has been removed; the greatest diminution observed was from 0·80 to 0·50 per cent. in eight days.

C. F. B.

Preparation of 1-Phenyl- and *p*-Tolyl-naphthylamine-8-sulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 158923).—When α -naphthylamine-4:8-disulphonic acid is

heated with aniline or *p*-toluidine, with the addition of benzoic acid or aniline hydrochloride, for thirty hours at 180°, the phenyl or *p*-tolyl enters the amino-group, the sulphonic group in the 4-position being at the same time replaced by hydrogen, so yielding 1-phenyl- (or *p*-tolyl-) naphthylamine-8-sulphonic acid. Other naphthylaminesulphonic acids do not react in this way. C. H. D.

Compounds of Ketones with Ammonia. Benzophenone Ammonia (Iminobenzophenone). CARL THOMAE (*Arch. Pharm.*, 1905, 243, 395—398. Compare this vol., i, 509).—A mixture of benzophenone with three times its weight of alcohol is saturated with gaseous ammonia and allowed to remain for several weeks in the dark. It is then exposed in a thin layer for evaporation. Finally the solid residue is powdered, and is either dissolved in ether and treated with an ice-cold saturated ethereal solution of hydrogen chloride, or is dissolved in chloroform, treated with a solution of hydrogen chloride in chloroform, and diluted with benzene. In both cases a white salt separates, which has the composition of iminobenzophenone hydrochloride, $\text{CPh}_2\text{:NH}\cdot\text{HCl}$ (Hantzsch and Kraft, *Abstr.*, 1892, 338). By adding an ethereal solution of picric acid to the solution of the crude product in ether, a *picrate* melting at 170° is obtained. A hydrobromide is obtained as an oily by-product of the action of bromine on the base in ethereal solution. These salts are unstable, especially in the presence of water, decomposing into benzophenone and ammonium salts. C. F. B.

New Indoline Bases. ALOIS PLANGGER (*Monatsh.*, 1905, 26, 833—838. Compare Brunner, *Abstr.*, 1900, i, 360).—3:3:7-*Trimethyl-2-methyleneindoline hydriodide*, $\text{C}_{12}\text{H}_{16}\text{NI}$, formed by treating the *o*-tolylhydrazone of methyl isopropyl ketone with alcoholic hydrogen iodide, crystallises in needles and melts at 185.5°. An impure *stannochloride* of the base, crystallising in long needles, is obtained by boiling the hydrazone with stannous chloride and alcoholic hydrogen chloride in a reflux apparatus. The free base, $\text{C}_7\text{H}_6\langle\text{CMe}_2\text{NH}\rangle\text{C:CH}_2$, liberated from the double salt by potassium hydroxide, is a yellow oil which boils at 158° under 20 mm. pressure, is volatile in a current of steam, and becomes brown on exposure to the air. The yellow, crystalline *picrate* melts and decomposes at 174°. When warmed with methyl iodide, the base forms the *hydriodide* of 1:3:3:7-tetramethyl-2-methyleneindoline, $\text{C}_{13}\text{H}_{18}\text{NI}$, which crystallises in white leaflets, melts and decomposes at 212°, and when treated with potassium hydroxide yields the base $\text{C}_7\text{H}_6\langle\text{CMe}_2\text{NMe}\rangle\text{C:CH}_2$. This is a colourless liquid which boils at 138° under 20 mm. pressure, becomes carmine on exposure to air, and forms crystalline salts. The *picrate* crystallises in lemon-yellow needles and melts at 165°; the *ferrichloride* forms whitish-brown, delicate needles melting at 113°, and is insoluble in concentrated hydrochloric acid. G. Y.

3-Ethylindole and 1:3:3-Triethyl-2-ethylideneindoline. GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 31—36).—3-Ethylindole, $C_6H_4 \begin{smallmatrix} <NH \\ >CEt \end{smallmatrix} CH$, prepared by the condensation of *n*-butaldehydephenylhydrazone in absolute alcoholic solution by means of zinc chloride, has a faecal odour and crystallises from light petroleum in colourless scales melting at 43° (compare Pictet and Duparc, *Abstr.*, 1888, 370). The picrate, $C_{10}H_{11}N, C_6H_3O_7N_3$, separates from a mixture of benzene and light petroleum in crystals melting at 114—115°; Pictet and Duparc (*loc. cit.*) gave the melting point 143°. **1:3:3-Triethyl-2-ethylideneindoline**, $C_6H_4 \begin{smallmatrix} <NEt \\ >CEt_2 \end{smallmatrix} C \cdot C_2H_5$, obtained, together with 2:3:3-triethylindoline, by the action of ethyl iodide on 3-ethylindole, boils at 187° under 40 mm. pressure, and has a faint sweetish aminic odour; it is colourless, but rapidly turns red. Its *picrate*, $C_{16}H_{23}N, C_6H_3O_7N_3$, separates from alcohol in crystals melting at 102—103°. T. H. P.

Relation between Quinonehydrazones and *p*-Hydroxyazo-compounds. II. **New Class of Hydroxyazo-compounds.** WALTHER BORSCHKE and K. A. OCKINGA (*Annalen*, 1905, 340, 85—109). Compare *Abstr.*, 1904, i, 1056).—Unlike the naphthaquinones, the quinones of the benzene series will not condense with aromatic hydrazines; with *as*-acylphenylhydrazines and semicarbazide, on the other hand, condensation does take place, but not with *as*-phenylalkylhydrazines. The products obtained by using formyl-, hippuryl-, and benzoylhydrazines have been studied; in all cases they behave as hydroxyazo-compounds, since they condense neither with hydroxylamine nor with a second molecule of the hydrazine.

Formylazo-*p*-hydroxybenzene, $OH \cdot C_6H_4 \cdot N_2 \cdot CHO$, prepared by treating benzoquinone with a solution of formylhydrazine in *N*/1 hydrochloric acid, crystallises in yellowish-brown needles melting and decomposing at 141—142°. **1-Formylazo-4-hydroxy-3-methylbenzene**, $OH \cdot C_6H_3Me \cdot N_2 \cdot CHO$, prepared from toluquinone, crystallises in yellow needles melting and decomposing at 168—169°. **1-Formylazo-4-hydroxynaphthalene**, prepared from α -naphthaquinone, is a brown, crystalline powder decomposing at 225°. **2-Formylazo-1-hydroxynaphthalene**, prepared from β -naphthaquinone, crystallises in pale brown needles melting and decomposing at 168°.

Hippurylazo-*p*-hydroxybenzene, $OH \cdot C_6H_4 \cdot N_2 \cdot CO \cdot CH_2 \cdot NHBz$, prepared from hippurylhydrazine hydrochloride and benzoquinone in dilute aqueous solution, is a reddish-yellow, crystalline powder, decomposing at 170°. **1-Hippurylazo-4-hydroxy-3-methylbenzene**, prepared from toluquinone, forms pale yellow crystals melting at 169—170°. **1-Hippurylazo-4-hydroxy-2-methyl-5-isopropylbenzene**, prepared from thymoquinone, crystallises in yellow needles melting and decomposing at 200°. **1-Hippurylazo-4-hydroxynaphthalene**, prepared from α -naphthaquinone, crystallises in pale yellow needles melting at 229°. **2-Hippurylazo-1-hydroxynaphthalene** crystallises in orange-red needles melting at 180—181°.

Benzoylazo-*p*-hydroxybenzene, prepared from benzoquinone and a

dilute solution of benzoylhydrazine hydrochloride, forms brown crystals melting and decomposing at $143-144^{\circ}$; it is reduced by phenylhydrazine to *s*-benzoyl-4-hydroxyphenylhydrazine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NHBz}$, which crystallises in needles melting and decomposing at 154° . The benzoylazo-compound forms an *additive compound* with benzenesulphinic acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{SO}_2\text{Ph})\cdot\text{NHBz}$, a white, crystalline powder melting at 102° . 1-Benzoylazo-3:5-dibromo-4-hydroxybenzene, prepared by bromination of benzoylazo-*p*-hydroxybenzene in acetic acid solution, crystallises in orange-red needles melting at 205° , and when treated with sodium hydroxide is decomposed, yielding 2:6-dibromophenol. 2:6-Dibromophenyl benzoate, prepared by the action of benzoyl chloride on the corresponding phenol in the presence of pyridine, crystallises in leaflets melting at 68° . 1-Benzoylazo-4-hydroxy-3-methylbenzene, prepared from toluquinone, crystallises in pale brown needles melting at $172-174^{\circ}$, and is reduced by phenylhydrazine to *s*-benzoyl-4-hydroxy-3-methylphenylhydrazine, which is a crystalline powder melting at 175° , and with benzenesulphinic acid forms an *additive product*, a colourless solid melting at 84° . 4-Benzoylazo-3-methylphenyl benzoate, prepared by benzoylation of the benzoylazo-*o*-cresol in the presence of pyridine, is a pale brown solid. 1-Benzoylazo-5-bromo-4-hydroxy-3-methylbenzene, prepared by brominating benzoylazo-*o*-cresol, crystallises in pale yellow needles melting at 209° . 1-Benzoylazo-4-hydroxy-2-methyl-5-isopropylbenzene, prepared from thymoquinone, forms dark yellow needles melting at $165-167^{\circ}$, and is reduced by phenylhydrazine to the corresponding hydrazo-compound, a crystalline powder melting at 167° . The azo-compound forms an *additive compound* with benzenesulphinic acid, melting at 130° .

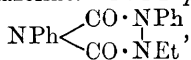
On brominating benzoylazo-thymol, 1-benzoylazo-3-bromo-4-hydroxy-2-methyl-5-isopropylbenzene is obtained as pale yellow crystals melting at 209° . 1-Benzoylazo-4-hydroxynaphthalene, prepared from α -naphthaquinone, crystallises in yellow needles melting at 220° , whilst the corresponding *derivative* of β -naphthaquinone forms dark red crystals melting at $180-182^{\circ}$.

K. J. P. O.

[Azine Derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158287).—On heating 2-chloro- or 2-bromo-1-aminoanthraquinone or their derivatives with metallic salts, such as cupric chloride or zinc chloride and sodium acetate in nitrobenzene or other indifferent solvent, condensation takes place, hydrogen chloride or bromide being removed and two anthraquinone groups combining to form an azine. The products form blue or green crystals, and dissolve in boiling aniline or nitrobenzene. Alkaline reducing agents convert them into blue or green dyes. C. H. D.

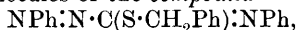
Some Urazole and Iminothiodiazoline Derivatives. HENRY L. WHEELER and JOANNES G. STATIROPOULOS (*Amer. Chem. J.*, 1905, 34, 117—132)—3-Ethoxy-1:4-diphenylurazole, $\text{NPh} \begin{array}{c} \text{CO}\cdot\text{NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{OEt}) \end{array} \text{N}$, obtained by the action of ethyl iodide on the silver derivative of 1:4-diphenylurazole, crystallises in long, slender prisms, softens at

83—85°, melts at 85—86°, and is identical with the compound regarded by Wheeler and Dustin (Abstr., 1901, i, 24) as 5-ethoxy-2-phenylimino-3-phenyloxydiazoline. 1:4-Diphenyl-2-ethylurazole,



prepared by the action of ethyl bromide on the sodium derivative of 1:4-diphenylurazole at 100°, crystallises in lustrous prisms, melts at 125—126°, and is readily soluble in alcohol, ether, or benzene, and moderately so in hot water.

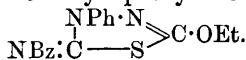
The additive compound, $\text{NHPh} \cdot \text{NH} \cdot \text{CCl}(\text{S} \cdot \text{CH}_2\text{Ph}) \cdot \text{NHPh}$, formed by the union of benzyl chloride with diphenylthiosemicarbazide, melts at 149—150°, and is readily soluble in alcohol. The free *diphenyl-ψ-benzylthiosemicarbazide* is very unstable and rapidly oxidises in the air. When an alcoholic solution of the benzyl chloride additive compound, cooled in a freezing mixture, is neutralised with dilute sodium hydroxide, a yellow oil is produced which, after several hours, furnishes bright red needles of the compound



melting at about 55°. When an ethereal solution of the free diphenyl-ψ-benzylthiosemicarbazide is treated with carbonyl chloride, 3-benzylthiol-1:4-diphenylurazole, $\text{NPh} \begin{array}{c} \text{CO} \text{---} \text{NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{S} \cdot \text{CH}_2\text{Ph}) \end{array} \text{N}$, is produced, which crystallises in long, slender, lustrous needles, melts at 110—112°, and is identical with the substance obtained by Wheeler and Dustin (*loc. cit.*) by the action of benzyl chloride on ethyl *c:b*-diphenyl-*a*-thiosemicarbazide in presence of alkali and regarded as 5-benzylthiol-2-phenylimino-3-phenyloxydiazoline.

5-Thio-3-ethoxy-1:4-diphenylurazole, $\text{NPh} \begin{array}{c} \text{CS} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{C}(\text{OEt}) \end{array} \text{N}$, obtained by the action of phenylthiocarbimide or phenyliminocarbonyl chloride on ethyl phenylthioncarbazinate, crystallises in large, rhombic prisms [$a:b:c = 0.9528:1.00:1.012$], melts at 83°, and is readily soluble in alcohol, less so in ether, and insoluble in water; when boiled with hydrobromic acid, it yields 5-thio-1:4-diphenylurazole.

By the action of benzoylthiocarbimide on ethyl phenylthioncarbazinate, Wheeler and Dustin (*loc. cit.*) obtained a compound which melted at 136—138° and was provisionally regarded as 5-thio-4-benzoyl-3-ethoxy-1-phenyltriazolone. It is now found that this substance is 2-benzoylimino-5-ethoxy-3-phenylthiodiazoline,

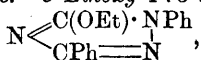


When the compound is boiled with hydrobromic acid, 5-oxo-1:3-diphenyl-triazole, $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{NPh} \\ \diagup \quad \diagdown \\ \text{CPh} : \text{N} \end{array}$, is produced, which crystallises in colourless needles, melts at 229—230°, and is soluble in ether, benzene, or hot alcohol, but only slightly so in boiling water; its constitution was proved by the following synthesis. When benzoylcarbimide is allowed to react with acetonephenylhydrazone, the *semicarbazone*,

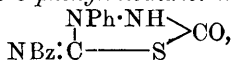


is formed, which crystallises in colourless, microscopic prisms, melts

at 139—140°, and is converted by warm dilute hydrochloric acid into 5-oxy-1:3-diphenyltriazole. 5-Ethoxy-1:3-diphenyltriazole,



obtained by the action of ethyl bromide on 5-oxy-1:3-diphenyltriazole in presence of potassium hydroxide, crystallises in lustrous, rhombic prisms, melts at 85—86°, and is readily soluble in alcohol, benzene, or ether, and slightly so in boiling water. When 2-benzoylimino-5-ethoxy-3-phenylthiodiazoline is heated at 140—145° in a current of hydrogen chloride, 2-benzoylimino-3-phenylthiodiazolone,



is produced, which crystallises in colourless needles, melts at 206—207°, and is readily soluble in hot alcohol and less so in ether, benzene, or hot water; its *sodium* and *silver* derivatives are described. When either of these derivatives is treated with ethyl iodide, 2-benzoylimino-5-ethoxy-3-phenylthiodiazoline is regenerated. The diazoline may also be obtained by the action of benzoyl isocyanochloride (Johnson and Menge, Abstr., 1904, i, 949) on ethyl phenylthioncarbazinate. Contrary to the statement of Wheeler and Dustin (*loc. cit.*), the compound is not desulphurised by silver nitrate; mercuric oxide is also without effect on it.

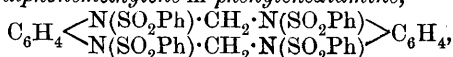
The following derivatives of 5-thio-1:3-diphenyltriazole (Wheeler and Beardsley, Abstr., 1902, i, 503) are described. 5-Methylthiol-1:3-

diphenyltriazole, $\text{N} \begin{array}{c} \diagup \text{C(SMe) \cdot NPh} \\ \diagdown \text{CPh} \end{array} \text{---} \text{N}$, crystallises in large, colourless

needles, melts at 56—57°, and is readily soluble in ether or benzene, and sparingly so in boiling water. 5-Ethylthiol-1:3-diphenyltriazole forms stout, colourless prisms, melts at 52—53°, and when dissolved in hydrobromic acid yields a salt melting at 152°. 1:3-Diphenyltriazole 5-disulphide, $(\text{C}_{14}\text{H}_{10}\text{N}_3)_2\text{S}_2$, crystallises in slender, colourless needles, melts at 182—183°, and is slightly soluble in ether or alcohol and insoluble in water. E. G.

Action of Alkylene Haloids on *m*- and *p*-Dibenzenesulphophenylenediamine. OSCAR HINSBERG and J. KESSLER (*Annalen*, 1905, 340, 110—121).—It has been shown by Hinsberg and Strupler (Abstr., 1896, i, 47) that diphenylsulphone-*o*-phenylenediamine gives cyclic compounds with methylene chloride, ethylene bromide, and trimethylene bromide. In the case of derivatives of *m*- and *p*-phenylenediamine, it has now been found that such cyclic compounds are not produced, but that substances belonging to a bimolecular type are formed.

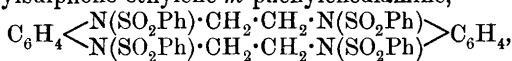
Bisdiphenylsulphonemethylene-m-phenylenediamine,



is prepared by heating diphenylsulphone-*m*-phenylenediamine with methylene chloride and sodium methoxide in alcohol under pressure at 110°; the compounds can be isolated from the product by repeated precipitation from solution in various solvents as an amorphous,

colourless powder, which becomes coloured at 64° and melts at 82—86° to a turbid liquid, which is clear at 110—120°; it is insoluble in acids and in alkali hydroxides.

Bisdiphenylsulphone-ethylene-*m*-phenylenediamine,



prepared in a similar manner, is a colourless powder, becoming brown at 85° and melting at 92—96° to a turbid liquid which becomes clear at 120°. The statements previously made regarding this compound (*loc. cit.*) are incorrect. *Bisdiphenylsulphonetrimethylene-*m*-phenylenediamine*, $\text{C}_{42}\text{H}_{40}\text{O}_8\text{N}_4\text{S}_4$, is an amorphous, colourless powder, becoming brown at 80° and melting at 102—108° to a turbid liquid which becomes clear at 125°. When heated at 150° with concentrated hydrochloric acid, it is converted into an amorphous base. *Bisdiphenylsulphonetrimethylene-*p*-phenylenediamine* is an amorphous, colourless powder, becoming brown at 60° and melting at 75—80° to a turbid liquid which becomes clear at 125°.

*Diphenylsulphonedithyl-*m*-phenylenediamine*, $\text{C}_6\text{H}_4(\text{NEt} \cdot \text{SO}_2\text{Ph})_2$, prepared from diphenylsulphone-*m*-phenylenediamine, ethyl iodide, and sodium ethoxide at 110°, forms colourless crystals melting at 105°; its molecular weight in naphthalene solution is normal.

K. J. P. O.

[Azo-dyes from β -Diketones and β -Ketonic Esters.] FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158148 and 160040).—Diazotised solutions of *o*-aminosalicylic acid and its substituted derivatives combine with the sodium derivatives of acetylacetone, benzoylacetone, ethyl acetoacetate, acetoacetanilide, and similar compounds, yielding yellow, crystalline dyes. The products form bright yellow lakes, of which the cupric lakes are the most remarkable.

Similar products are obtained when *o*-aminosalicylic acid is replaced by *o*-aminophenol or its substituted derivatives, such as *o*-aminophenolsulphonic acid or 6-nitro-2-aminophenol-4-sulphonic acid.

C. H. D.

Oxidation of *o*-Phenylenediamine. RICHARD WILLSTÄTTER and ADOLF PFANNENSTIEL (*Ber.*, 1905, **38**, 2348—2352. Compare Griess, *J. pr. Chem.*, 1871, [ii], **3**, 142; O. Fischer and Hepp, *Abstr.*, 1889, 499; 1890, 800, 1440; O. Fischer and O. Heiler, *Abstr.*, 1893, i, 266; O. Fischer and O. Jonas, *Abstr.*, 1895, i, 25; O. Fischer, *Abstr.*, 1904, i, 349; Ullmann and Mauthner, *Abstr.*, 1903, i, 199; 1904, i, 192).—Silver oxide and lead peroxide react with an ethereal solution of *o*-phenylenediamine in the absence of moisture yielding a pale yellow solution which presumably contains *o*-quinonedi-imine. When warmed or shaken with hydrochloric acid, the colour of the ethereal solution turns to deep red and then contains diaminophenazine and *o*-azoaniline. These products may be readily separated, as the diaminophenazine is completely removed by shaking the ethereal solution with water.

o-Azoaniline (2:2'-diaminoazobenzene), $\text{N}_2(\text{C}_6\text{H}_4\text{NH}_2)_2$, is most readily purified by conversion into the sulphate. The best yields are

obtained by boiling the oxidised ethereal solution for some hours. It crystallises from hot alcohol or benzene in copper-red plates with a metallic lustre and melts at 134° . Dilute solutions have a pale yellow and concentrated solutions a yellowish-red colour. With acids, it gives no characteristic colour changes (compare Nietzki, Abstr., 1884, 740). The *hydrogen sulphate*, $C_{12}H_{12}N_4 \cdot 2H_2SO_4$, crystallises in long, yellow prisms, and is sparingly soluble in water. *o-Azoacetanilide* forms long, orange-yellow prisms melting at 271° . *o*-Phenylenediamine forms an *additive compound* with silver nitrate, $C_6H_8N_2 \cdot AgNO_3$; this is stable in the dry state, but when warmed with water, metallic silver is deposited and diaminophenazine nitrate is formed. J. J. S.

Rate of Decomposition of Diazonium Salts. JOHN C. CAIN (*Ber.*, 1905, 38, 2511—2517).—Schwalbe's contention (this vol., i, 618) that the conclusions of Cain and Nicoll (*Trans.*, 1902, 81, 1412) were based on the rate of decomposition of diazonium salts with absolutely pure bases and could not accordingly hold for technical diazo-solutions is incorrect.

The author has now studied the decomposition of benzenediazonium chloride in acetic acid solution; the effect of other acids on the decomposition of diazonium salts has also been examined. Hydrochloric acid in varying concentrations has no influence on the rate of decomposition of benzenediazonium chloride. Sulphuric acid, on the other hand, has an effect when the concentration of the acid is increased, giving rise to a secondary reaction. Equivalent solutions of benzenediazonium chloride, sulphate, nitrate, and oxalate respectively are decomposed at the same rate. A. MCK.

Reaction of Aromatic Azo-compounds with Aromatic Amines differing from the Induline Synthesis. ARTHUR WEINSCHENK (*Zeit. Farb. Text. Ind.*, 1905, 4, 337—339).—The action of 1 mol. of azobenzene on 1 mol. of α -naphthylamine in warm 70 to 80 per cent. sulphuric acid solution leads to the formation of benzidine and a *base* which, on treatment with a small quantity of zinc dust in dilute acid solution and precipitation with ammonia, is obtained as a yellowish-white mass, becoming grey on warming or drying in air, and containing C=82.3; H=5.8; N=11.7 per cent. It is easily soluble in dilute sulphuric or hydrochloric, glacial acetic, or hot dilute oxalic acid, but is only slightly soluble in most organic solvents and is almost insoluble in hot dilute acetic acid or water. With acetic anhydride, the base forms an *acetyl* derivative insoluble in dilute acids; with sodium nitrite in hydrochloric acid, it yields an insoluble *polydiaz*-derivative, which, with a further quantity of sodium nitrite, forms a brown *nitrosodiazo*-solution. This combines with 2 mols. of the usual azo-dye components to form derivatives which dye unmordanted cotton-wool. With sodium naphthionate or β -naphthylamine-5-sulphonate in presence of sodium acetate, the nitrosodiazo-solution forms intermediate products, which contain a free diazo-group and form mixed azo-dyes with *H*-acid in alkaline solution. The base derived from azobenzene and α -naphthylamine must contain the group

$\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2$. The reaction by which it is formed is capable of extension to other aromatic azo-compounds and aromatic amines.

G. Y.

Tetrazophenolsulphonic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 158532).—*m*-Phenylenediaminedisulphonic acid is converted by an excess of nitrous acid at 15° into a *tetrazophenolsulphonic acid*, which separates in yellow crystals. One sulpho-group is thus replaced by hydroxyl.

C. H. D.

Colouring Matter of Blood. V. H. GOLDMANN, J. HEPTER, and LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, 45, 176—182. Compare this vol., i, 399).—The azo-dye previously described is *hæmopyrroledisazobenzene hydrochloride*, $\text{C}_{20}\text{H}_{22}\text{N}_5\text{Cl}$. In the powdered state it melts at 233° , and is only sparingly soluble in ether, benzene, or chloroform. Its solution in concentrated sulphuric acid has at first a bluish-violet colour, but this changes to reddish-violet. The solution in alcoholic potash has a more reddish colour. The spectroscopic properties are not specially characteristic. *Hæmopyrrole* and toluene-diazonium chloride yield the *hydrochloride* of an *azo-dye*, $\text{C}_{22}\text{H}_{26}\text{N}_5\text{Cl}$, in the form of dark brown, glistening needles melting at 254° .

J. J. S.

State of Combination of Sulphur in Proteids. PAUL N. RAIKOW (*Chem. Zeit.*, 1905, 29, 900—901).—Twenty grams of carefully washed unbleached wool, placed in a stoppered bottle of 300 c.c. capacity with phosphoric acid of sp. gr. 1.7, becomes brown after sixteen hours, and on removing the stopper a strong odour of sulphur dioxide is noticed. After two months, the contents of the bottle are changed to a dark brown, thick, homogeneous liquid and evolve a very powerful odour of sulphur dioxide; only a very small additional amount is formed on setting aside the bottle for a few more days. In the author's opinion, this proves that part of the sulphur in keratin is combined directly with oxygen. Human hair behaves in much the same way as wool, although the action is somewhat slower. One gram of each of the following substances, sulphuric acid, potassium methyl sulphate, sulphanilic acid, and the mono- and di-sulphonic derivatives of salicylic acid, allowed to remain for ten days in stoppered bottles with 20 c.c. of phosphoric acid, did not in any case evolve sulphur dioxide. The conclusion is reached that the sulphur in the proteid molecule is not combined in the form of a sulphate or a sulphonic acid, but more probably is present in part in a sulphite-like form.

P. H.

Oxidations with Calcium Permanganate. Reply to Kutscher and Seemann. RICHARD BURIAN (*Zeit. physiol. Chem.*, 1905, 45, 351—354. Compare Abstr., 1904, i, 127; this vol., ii, 271).—Polemical.

J. J. S.

Fibrinoglobulin. WOLFGANG HEUBNER (*Zeit. physiol. Chem.*, 1905, 45, 355—356).—A reply to Huiskamp (this vol., i, 499). It is

probable that Huiskamp's fibrinoglobulin solutions contained albumins and fibrinogen unless they were prepared by Hammarsten's method with neutral plasma. J. J. S.

Substances Extracted from Muscle. II. Carnitine. WLADIMIR VON GULEWITSCH and R. KRIMBERG (*Zeit. physiol. Chem.*, 1905, 45, 326—330. Compare Abstr., 1900, i, 516).—A new base, *carnitine*, is precipitated by the addition of potassium bismuth iodide solution to the filtrate from the precipitation of carnosine as its silver derivative. It has been obtained as the *platinichloride*, $C_{14}H_{32}O_6N_2Cl_6Pt$, in the form of minute, orange-red needles which melt and decompose at 214—218°. The base is strongly alkaline and dissolves readily in water, as do also the *hydrochloride* and *nitrate*. The latter crystallises in needles and has $[\alpha]_D$ about -22° . J. J. S.

Isolation of Lysine. ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, 45, 77—78).—Lysine is precipitated by mercuric chloride in the presence of barium hydroxide. In the separation of lysine from arginine and histidine, the latter are precipitated by the addition of silver nitrate and baryta, the excess of silver is removed from the filtrate, and the lysine precipitated by the addition of mercuric chloride. To obtain the base, the well-washed precipitate is suspended in dilute hydrochloric acid and decomposed with hydrogen sulphide. The filtrate when evaporated leaves the base as a syrup. J. J. S.

Peptones. WALTER NEUMANN (*Zeit. physiol. Chem.*, 1905, 45, 216—251. Compare Siegfried, Abstr., 1903, i, 782).—The molecular conductivities of aqueous solutions of pepsin-fibrinpeptone- α , of anti-peptone- α , and of anti-peptone- β have been determined, but, as with certain other amphoteric electrolytes, dissociation constants cannot be obtained by Ostwald's dilution law. The concentration of the hydrogen ions in aqueous solutions of peptones has been determined by Löwenherz' method (Abstr., 1896, ii, 587). The results indicate that a $N/16$ solution of pepsin-fibrinpeptone is only 0.0002*N* as regards hydrogen ions, whereas a $N/16$ solution of acetic acid is 0.00105*N* as regards hydrogen ions.

The peptones themselves in aqueous solution can precipitate gold from its colloidal solutions.

The equivalents of certain acids have been determined by mixing a given volume of the acid solution of known concentration with the same volume of much more dilute standard alkali hydroxide and determining the specific conductivity of the partially neutralised solution; to the mixture is added its own volume of the alkali solution and the conductivity again determined. The operation is repeated and the results plotted in the form of a curve of which the co-ordinates represent specific conductivities and concentration of the acid. With a strong acid and strong base, the curve consists of two straight lines meeting at a eutectic point which represents the equivalent weight of the acid. With a weak acid or alkali, a hyperbolic curve is given, one limb of which runs practically parallel with the concentration co-ordinate. In this case, the equivalent of the acid is given by the

point of intersection of the asymptotes to the curve. The method has been tried for telluric acid, glycine, and asparagine, using sodium hydroxide solutions of different concentrations, and also for creatine, glycine, and asparagine, as bases using hydrochloric acid of known strength.

In the latter experiments, the values obtained are rather high, especially with the more dilute solutions, owing to the high degree of hydrolysis. The same method has been used for determining the equivalents of some of Siegfried's pure peptones, using both sodium hydroxide and also hydrochloric acid solutions. The numbers obtained are :

	With NaOH.	With HCl.	Ratio.
Pepsin-fibrinpeptone- α	248	370	2 : 3
Pepsin-glutininpeptone- α	320	470	2 : 3
Antipeptone- α	157	290	1 : 2
Antipeptone- β	197	397	1 : 2

It is thus probable that the antipeptones are dibasic acids, but monoacidic bases, and the other two peptones tribasic acids and diacidic bases.

A discussion of probable molecular weights of certain peptones follows.

The numbers previously obtained by Calvert (*Trans.*, 1902, 81, 10) indicate that in dilute solutions hydrogen peroxide behaves as a monobasic acid and gives salts of the type NaHO_2 . J. J. S.

Peptones. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1905, 45, 252—257. Compare preceding abstract).—When aspartic and glutamic acids are treated with a slight excess of barium hydroxide and carbon dioxide passed into the solution until it is faintly acid, then boiled and evaporated in a platinum dish, barium hydrogen salts of the type $[\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2]_2\text{Ba}$ are obtained. The peptones yield barium salts in a similar manner, and it should follow that these are acid salts, and the equivalents determined from the barium salts must thus be greater than those from the titration and conductivity method, but the two should bear a simple relationship. This is shown to hold good for trypsin-fibrinpeptones- α and - β , pepsin-fibrinpeptone- α and pepsin-glutininpeptone. J. J. S.

Proteids obtained from Ricinus Seeds. ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1905, 45, 69—76).—The proteid extracted from *Ricinus* seeds by Ritthausen's method contains only 13.6 per cent. of nitrogen, and when hydrolysed with concentrated hydrochloric acid yields various bases. A new base isomeric with lysine has been isolated from the lysine fraction. The *dihydrochloride* of the new base is insoluble in boiling methyl alcohol. It sinters at 155° , melts at 160° , and decomposes at 162° ; it is optically active and has $[\alpha]_D +12.9^\circ$. It yields no precipitates with picric acid, gold chloride, platinic chloride, mercuric chloride or sulphate, tannic acid, or potassium mercuri-iodide. With phosphotungstic acid, it yields a white precipitate which dissolves on warming; with phosphomolybdic acid a

yellow precipitate, with Nessler's reagent a white precipitate, and a similar one with mercuric chloride and alkali hydroxide. Its most characteristic reaction is the glistening, dark red, crystalline precipitate yielded with potassium bismuth iodide. The amount of the new base is extremely small; from 200 grams of proteids only 0.3 gram of the hydrochloride was obtained, and the amount appears to vary with different samples of seeds. J. J. S.

Cause of the Fluorescent Reaction of Bile Acids with Sulphuric Acid. FRITZ PREGL (*Zeit. physiol. Chem.*, 1905, 45, 166—175).—When dry cholic acid is heated with glacial acetic and concentrated sulphuric acids, a product is obtained from which two substances have been isolated: (1) a colourless acid insoluble in water but soluble in sulphuric acid to a non-fluorescent solution, and (2) a neutral substance, *dehydrocholone*, $C_{24}H_{28}O$ or $C_{23}H_{27}O$, which dissolves in concentrated sulphuric acid, yielding an orange-red solution with a green fluorescence. It is readily soluble in most organic solvents, but insoluble in water, acids, or alkalis. It has not been obtained in a crystalline form, melts at 90—100° to a brown, transparent liquid, and with nitric acid yields a dinitrodicarboxylic acid.

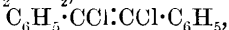
An examination of the molecular refraction and dispersion of cholic acid leads to the conclusion that no ethylenic (or benzene) linkings are present in the molecule, whereas with dehydrocholone the presence of such linkings is highly probable. The heat of combustion of cholic acid is 8103 cal. per gram. J. J. S.

Philothionic Hydrogen. JOSEPH DE REY-PAILHADE (*Bull. Soc. chim.*, 1905, [iii], 33, 850—854. Compare Abstr., 1904, i, 837).—When pseudo-philothion is heated at 120—130° for some fifteen hours it loses the property of being able to reduce sulphur; this is attributed to the action of the atmospheric oxygen on the philothionic hydrogen. When dry pseudo-philothion is heated with sulphur at 120° for four hours, hydrogen sulphide is formed in quantity, but if the experiment is repeated while a slow stream of air is passed over it, only traces of sulphide are formed.

At the ordinary temperature, the philothion from ovalbumin is not readily destroyed by atmospheric oxygen, does not decolorise sodium indigotinsulphonate, or methylene-blue, and is only very slowly acted on by hydrogen peroxide at the ordinary temperature. Boiling with acidified hydrogen peroxide destroys philothion, as does nitrous acid. The question of the presence of hydrogen sulphide in various foods is discussed. J. J. S.

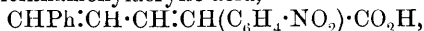
Organic Chemistry.

Nature of the Carbon Double Linking. HUGO BAUER (*J. pr. Chem.*, 1905, [ii], 72, 201—210. Compare *Abstr.*, 1904, i, 841).—The addition of bromine to unsaturated carbon compounds is affected by the presence of chlorine atoms and of nitrile groups in the same manner as by that of phenyl or carboxyl groups or of bromine atoms. Tetrachloroethylene, $\text{CCl}_2\text{:CCl}_2$, and dichlorostilbene,

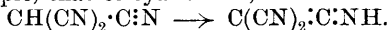


for example, do not form additive compounds with bromine. The nitrile group affects the addition of bromine to a greater extent than does the carboxyl group, whilst this has a greater effect than the phenyl group. Thus, α -phenylcinnamitrile, $\text{CHPh}\text{:CPh}\cdot\text{CN}$, forms a dibromide, but ethyl benzylidenemalonate, $\text{CHPh}\text{:C}(\text{CO}_2\text{Et})_2$, decolorises bromine to only a slight extent, and α -cyanocinnamic esters, $\text{CHPh}\text{:C}(\text{CN})\cdot\text{CO}_2\text{R}$, do not unite with bromine. The tendency to add bromine diminishes as the negative nature of the substituting groups increases; thus addition of bromine is no longer possible if a nitro-group is introduced into the para-position in either of the phenyl groups of α -phenylcinnamitrile; if the nitro-group is introduced into an ortho-position, the behaviour of the resulting product resembles that of ethyl benzylidenemalonate, whilst a nitro-group in the meta-position has no influence on the behaviour towards bromine.

If unsaturated carbon compounds with one double linking are considered to contain two tervalent carbon atoms which become quadri-valent on formation of additive compounds, carbon forms an exception to the general rule that elements act with higher valencies the more negative the groups or atoms to which they are attached. The protection of a double linking by neighbouring negative groups explains the formation of 3:4- instead of 1:4-dibromo-additive compounds from such substances, containing conjugated ethylene linkings, as *p*-nitrophenylcinnamylacrylic acid,



and cinnamylidenemalonic esters, $\text{CHPh}\text{:CH}\cdot\text{CH}\text{:C}(\text{CO}_2\text{R})_2$. To the negative influence of the substituting groups are due such cases, as with *s*-diphenylethylene, in which bromine is added, but the additive compound immediately loses hydrogen bromide and forms an unsaturated compound, as also certain cases of intramolecular change, for example, that of cyanoforn,



G. Y.

New Heptane: $\beta\delta$ -Dimethylpentane. G. CHONIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 521—523).—Saturation of dimethylisobutylcarbinol with hydrogen iodide yields the corresponding iodide, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\text{I}$, which boils and decomposes slightly at 140—142° under 756 mm. pressure. When heated with hydriodic acid in a

sealed tube at 220—230°, this iodide is converted into $\beta\delta$ -dimethyl-pentane, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$, which boils at 83—84° under 764 mm. pressure, has the sp. gr. 0.6971 at 0°/0° and 0.6805 at 20°/0°, and n_D 1.3825 at 20°.

T. H. P.

Preparation of Hexachloroethane. KARL A. HOFMANN and E. SEILER (*Ber.*, 1905, **38**, 3058—3059. Compare Kolbe, *Annalen*, **54**, 147; Goldschmidt, *Ber.*, 1881, **14**, 928; Radziszewski, *ibid.*, 1884, **17**, 834).—Carbon tetrachloride is heated with aluminium amalgam at 70° in a reflux apparatus and then poured into twice its volume of ice-water. The unaltered carbon tetrachloride is then distilled off and at 100° hexachloroethane passes over with the steam and may be extracted with ether. From 100 grams of the tetrachloride, 35 grams were recovered and 42 grams of hexachloroethane were obtained. When treated in a similar manner, chloroform deposits carbon, and hydrogen is evolved, whilst aluminium chloride goes into solution.

J. J. S.

Oxidising Action of Ferric Chloride in Sunlight. ALFRED BENRATH (*J. pr. Chem.*, 1905, [ii], **72**, 220—227).—A number of substances were mixed with sublimed ferric chloride in a sealed tube and exposed to bright sunlight. Under these conditions methyl alcohol and ferric chloride form methyl chloride, formaldehyde hydrochloride, hydrogen chloride and, if anhydrous, ferrous chloride methyl alcoholate, $\text{FeCl}_2\cdot 4\text{CH}_3\text{O}$, but if in presence of moisture, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$. Formaldehyde and ferric chloride in presence of water form formic acid, hydrogen chloride, and ferrous chloride, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$. Trioxymethylene and ferric chloride form an unstable, dark violet additive compound, but no oxidation of the trioxymethylene takes place. The action of ferric chloride on formic acid leads to the formation of carbon dioxide and hydrogen chloride. Absolute ethyl alcohol and ferric chloride yield acetaldehyde, ethyl chloride, hydrogen chloride, and ferrous chloride, $\text{FeCl}_2\cdot 2\text{H}_2\text{O}$ or $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, if 95 per cent. alcohol is used. Ether is oxidised to acetaldehyde hydrochloride, hydrogen chloride, and a substance which may be a mixture of butane and ethyl chloride. With anhydrous ether, anhydrous ferrous chloride, but in presence of water $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, is formed. In presence of water, acetaldehyde is oxidised to acetic acid, hydrogen chloride and ferrous chloride, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, being formed; but if anhydrous substances are used, the aldehyde is converted into resin.

Acetic acid and ferric chloride form a rose-red powder. The action of ferric chloride on dimethylethylcarbinol is that of a dehydrating agent.

G. Y.

Spontaneous Oxidation of Ethyl Alcohol. L. MATHIEU (*Chem. Centr.*, 1905, ii, 782; from *Bull. Assoc. Chim. Sucr. Dist.*, 1905, **22**, 1283—1293).—Aldehyde is formed in wines and other alcoholic liquids of similar concentration by simple contact with the air without the interaction of porous substances or micro-organisms.

The process is accelerated by the presence of oxidisable substances, such as sulphur dioxide, ferrous sulphate, ferrous oxide, manganous oxide, &c. Sunlight has the same effect, and green glass containing-vessels favour the oxidation. The phenomenon is subjected to a theoretical discussion.

H. M. D.

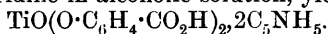
Action of Stannic and Titanic Chlorides on Organic Hydroxyl Compounds. ARTHUR ROSENHEIM and RICHARD SCHNABEL (*Ber.*, 1905, 38, 2777—2782. Compare Pfeiffer, this vol., ii, 594).—Compounds of the type $\text{SnCl}_2(\text{OMe})_2, \text{HCl}$, $\text{SnCl}_2(\text{OEt})_2, \text{HCl}$, $\text{SnCl}_2(\text{OPr})_2, \text{HCl}$,

and $\text{SnCl}_2(\text{OPh})_2, \text{HCl}$ have been obtained by the addition of stannic chloride to an excess of the well-cooled alcohol and partial evaporation of the solution. The compounds are all colourless, crystalline, and hygroscopic. The *propyl* compound melts at 163° . With alcohol in a good freezing mixture, stannic chloride yields the compound $\text{SnCl}_4 \cdot 2\text{EtOH}$.

Stannic chloride reacts with a hot chloroform solution of salicylic acid yielding the crystalline product $\text{SnCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2, \text{HCl}$, which melts at 150° . It is relatively stable and readily soluble in alcohol. With pyridine, the salt $\text{SnCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot 2\text{C}_5\text{NH}_5$ is obtained, and the complex $\text{SnCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2$ has thus an amphoteric character.

Pfeiffer's compounds are also regarded as hydrochlorides.

The following compounds have been obtained from titanic chloride: $\text{TiCl}(\text{OPr})_3, \text{HCl}$; $\text{TiCl}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_3, \text{HCl}$ (compare Demarcay, *Compt. rend.*, 1874, 80, 51). With the bromide, similar compounds, for example, $\text{TiBr}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_3, \text{HBr}$, have been prepared. The compounds react with pyridine in alcoholic solution, yielding



J. J. S.

Sodium Derivatives of Normal Propylene Glycol. ERNESTO PARONE (*Chem. Centr.*, 1905, ii, 751; from *Boll. Chim. Farm.*, 1905, 44, 481—483).—To obtain the mono-sodium compound, propylene glycol is treated with sodium amalgam, the product warmed with amyl alcohol, dissolved in boiling ethyl alcohol, and the solution distilled in a current of hydrogen. On cooling the residual solution, crystals of the formula $\text{C}_3\text{H}_7\text{O}_2\text{Na} \cdot \text{EtOH}$ separate. This substance deliquesces in the air and gradually decomposes, but can be kept in a sealed tube filled with hydrogen. When heated at 170° under diminished pressure, it gradually loses ethyl alcohol and a white porous mass remains.

The di-sodium compound, $\text{C}_3\text{H}_6\text{O}_2\text{Na}_2$, is obtained by adding gradually sodium dissolved in alcohol to a solution of the mono-sodium compound in alcohol and heating for three hours in a current of hydrogen.

Another method consists in treating a solution of the glycol in absolute alcohol with sodium ethoxide. The former method gives a 23, the latter a 94 per cent. yield. Hard, white, porous, hygroscopic masses are obtained, which decompose at 210 — 245° and must be kept in an atmosphere of hydrogen.

H. M. D.

Ketonic Alcohols. ANDRÉ KLING (*Ann. Chim. Phys.*, 1905, [viii], 5, 471—559).—For the most part a *résumé* of work already published (Abstr., 1899, i, 323; 1900, i, 129; 1901, i, 625; 1903, i, 138, 223; 1904, i, 2, 133, 474; this vol., i, 3, 172, 327, 503, 504, 625).—Acetylcarbinyl formate has a sp. gr. 1.1322 at 15°/15° and n_D 1.4206 at 15°. The *propionate* boils at 152—156° and yields a *hydrazone* melting at 189—190°. The *stearate* crystallises in unctuous scales, melts at 49—50°, and is soluble in alcohol and ether, slightly so in water.

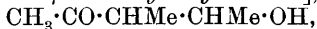
Attempts were made to determine the velocity of esterification of acetylcarbinol by acetic acid, but these had to be abandoned owing to the difficulty of titrating the free acetic acid in presence of acetylcarbinol, which behaves as a pseudo-acid: the initial velocity appears to be about 3.98.

Neither acetylcarbinol nor acetylmethylcarbinol is fermented by *Mycoderma aceti*, yeast, or *Aspergillus niger*, but *Penicillium glaucum* darkens the colour of a solution of acetylmethylcarbinol and induces a dextrorotation, which reaches a maximum and eventually disappears (at the same time as the ketone alcohol) if the fermentation is allowed to proceed for a long enough period.

Benzoylcarbinol, prepared by heating bromoacetophenone with potassium formate and methyl alcohol in a closed tube, behaves towards reducing and oxidising agents in a manner precisely analogous with that of the aliphatic ketone-alcohols. It differs from them principally in not being obtainable by the biological oxidation of the corresponding glycol.

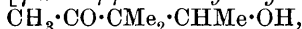
T. A. H.

Condensation of Aldehydes with Ketones in Presence of Potassium Cyanide. JULIUS SALKIND (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 484—492. Compare Claisen, Abstr., 1899, i, 667).—*Methylpentanonol* [γ -*keto*- $\alpha\beta$ -*dimethylbutyl alcohol*],



prepared by the condensation of methyl ethyl ketone with acetaldehyde in presence of potassium cyanide, boils at 82—83° under 16 mm., at 74—75° under 10 mm., and at 186—188° under the ordinary pressure, and has the sp. gr. 0.9779 at 0°/4° and 0.9651 at 17°/4°. The *semicarbazone*, $\text{C}_7\text{H}_{15}\text{O}_2\text{N}_3$, melts at 172.5—173° and dissolves moderately readily in alcohol or water. On reduction with sodium amalgam, methylpentanonol yields the corresponding *glycol*, $\text{OH} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{OH}$, which boils at 103—105° under 10 mm., at 113—115° under 20 mm., and at 211—212° under the ordinary pressure, and has the sp. gr. 0.9762 at 0°/4° and 0.9628 at 18°/4°. Oxidation of methylpentanonol with permanganate yields almost exclusively acetic acid (compare Zelinsky and Zelikoff, Abstr., 1901, i, 657).

Dimethylpentanonol [γ -*keto*- $\alpha\beta\beta$ -*trimethylbutyl alcohol*],



prepared by the condensation of methyl isopropyl ketone with acetaldehyde in presence of potassium cyanide, boils at 79—80° under 10 mm. pressure and has the sp. gr. 0.9786 at 4°/0° and 0.9676 at 13.5°/4°. The *semicarbazone*, $\text{C}_8\text{H}_{17}\text{O}_2\text{N}_3$, separates in stellar, crys-

talline aggregates melting at 127° , and dissolves readily in alcohol, water, or acetone. Oxidation of dimethylpentanonol with chromic acid in acetic acid solution yields dimethylacetylacetone, which was identified by means of its *disemicarbazone*, $C_9H_{18}O_2N_6$, melting at $227-228^{\circ}$.
T. H. P.

Compounds of Gold with Organic Sulphur Groups. FELIX HERRMANN (*Ber.*, 1905, **38**, 2813—2825).—When 3 mols. of a mercaptan are added to an alcoholic solution of 1 mol. of auric chloride, the auric mercaptide is formed as a brown precipitate which becomes white, whilst the colourless filtrate contains hydrochloric acid and the disulphide corresponding with the mercaptan.

Aurous isoamylmercaptide, $Au \cdot SC_5H_{11}$, forms a cryptocrystalline powder which is stable on exposure to air or light, decomposes at about 150° , with formation of metallic gold and an oily distillate, and is sparingly soluble in boiling toluene. *Aurous benzylmercaptide*, $Au \cdot SC_7H_7$, decomposes at $190-200^{\circ}$ and is almost insoluble in boiling toluene. The action of 2 mols. of dibenzyl sulphide on 1 mol. of auric chloride or ammonium aurichloride in alcoholic or ethereal solution leads to the formation of a voluminous, orange precipitate, consisting of spherical aggregates of needles, which changes after some days, or quickly on warming, into *aurodibenzylsulphine chloride*, $AuS(C_7H_7)_2Cl$, which is obtained as a heavy, crystalline powder. This is dimorphous, and crystallises from its hot saturated solution in alcohol or chloroform, on cooling in tetragonal needles, or on slow evaporation of its solutions at temperatures below 25° in monoclinic crystals resembling rhombohedra. It melts and decomposes at 122° , and becomes yellow on exposure to air, or violet in absence of air and light; in chloroform solution it yields, with hydrogen sulphide, a precipitate of auric sulphide, with mercaptans, precipitates of aurous mercaptides, and with potassium cyanide, benzyl sulphide and potassium auricyanide. The action of potassium iodide on auric dibenzylsulphine chloride leads to the production of benzyl sulphide, metallic gold, and potassium aurichloride and chloride; of silver nitrate, to the formation of aurous oxide, silver chloride, gold, and benzyl sulphide; of aqueous or alcoholic ammonia, to the formation of auriamine chloride, $AuNH_3Cl$. This is obtained as a white, cryptocrystalline precipitate, decomposes at $150-200^{\circ}$, and is formed also by the action of aqueous ammonia on auric chloride.

Auric dibenzyl sulphide dichloride, $S(C_7H_7)_2 : AuCl_2 \cdot AuCl_2 : S(C_7H_7)_2 ?$, which is the intermediate product in the formation of aurodibenzylsulphine chloride, is obtained by the action of 3 mols. of benzyl sulphide on 2 mols. of auric chloride in ethereal solution. It crystallises in delicate, glistening, orange needles, is stable when exposed to light or air, melts and decomposes at 127° , and dissolves in boiling chloroform to form a yellow solution, but is only sparingly soluble in ether or alcohol. On addition of alcoholic ammonia to the chloroform solution, it forms an amorphous precipitate which, when dry, explodes on being heated; with hydrogen sulphide, it forms a black precipitate of auroauric sulphide, and when treated with alcoholic potassium hydroxide yields a black precipitate of metallic gold. The action of

chlorine on auric dibenzyl sulphide chloride in chloroform solution leads to the formation of a yellow solution, whilst with bromine a product, $\text{AuBr}(\text{Cl}) \cdot \text{S}(\text{C}_7\text{H}_7)_2$?, is obtained, which crystallises in dark red needles.

The ethereal filtrate from the preparation of auric dibenzyl sulphide dichloride contains dibenzylsulphine oxide, $\text{O}:\text{S}(\text{C}_7\text{H}_7)_2$, melting at 133° . The action of hydrogen chloride on a mixture of this and auro-dibenzylsulphine chloride in chloroform solution leads to the formation of auric dibenzyl sulphide dichloride. The mechanism of the reactions by which these substances are formed is discussed. G. Y.

Action of Concentrated Feeble Acids on Metallic Chlorides.

ALFRED BENRATH (*J. pr. Chem.*, 1905, [ii], 72, 228—237. Compare this vol., ii, 705).—The product obtained by treating a metallic chloride with a concentrated feeble acid is usually a double salt.

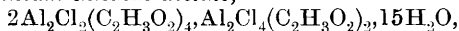
Ferric chloride formate, $\text{Fe}_2\text{Cl}_2(\text{CHO}_2)_4 \cdot \text{H}_2\text{O}$, crystallises from a solution of ferric chloride in warm formic acid, on cooling, in small, canary-yellow crystals; it dissolves in warm alcohol, glacial acetic acid, or water to form reddish-brown solutions, and when boiled with water yields a reddish-brown, basic salt. When heated at 110° , it is converted into a brownish-red powder, $\text{Fe}_2\text{Cl}_6 \cdot 14\text{Fe}_2\text{O}_3 \cdot 18\text{H}_2\text{O}$, which dissolves in hot hydrochloric acid and forms sodium chloride with boiling aqueous sodium hydroxide.

Ferric chloride acetate, $3\text{Fe}_2\text{Cl}_2(\text{C}_3\text{H}_3\text{O}_2)_4 \cdot \text{C}_2\text{H}_4\text{O}_2 \cdot 2\text{H}_2\text{O}$, formed by dissolving ferric chloride in glacial acetic acid, crystallises in small, red rhombohedra, when heated melts and evolves hydrogen chloride, and is easily soluble in water, alcohol, or ether.

Ferric chloride chloroacetate, $\text{Fe}_2\text{Cl}_2(\text{C}_2\text{H}_2\text{O}_2\text{Cl})_4 \cdot \text{H}_2\text{O}$, formed by fusing ferric chloride with chloroacetic acid, separates, on cooling, in crystals, and decomposes at 100° .

Ferric chloride propionate, $\text{Fe}_2\text{Cl}_2(\text{C}_3\text{H}_5\text{O}_2)_4$, crystallises from a mixture of ferric chloride and propionic acid in ruby-red crystals. If ferric chloride is boiled in an excess of propionic acid in a reflux condenser, it is reduced partly to ferrous chloride.

Aluminium chloride formate, $\text{Al}_2\text{Cl}_2(\text{CHO}_2)_4 \cdot 2\text{CH}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$, formed when aluminium chloride is dissolved in formic acid at 60° , separates as a loose, white, deliquescent powder, which has a strong acid reaction. *Aluminium chloride acetate*,



formed by the action of glacial acetic acid on powdered aluminium chloride or by boiling crystalline aluminium chloride with glacial acetic acid, forms a loose, white, hygroscopic powder, and dissolves in alcohol or water to form solutions with a strongly acid reaction. *Aluminium chloride propionate*, $\text{Al}_2\text{Cl}_2(\text{C}_3\text{H}_5\text{O}_2)_4$, formed by boiling powdered, sublimed aluminium chloride with an excess of propionic acid, is deliquescent, and when exposed to moist air has a strong odour of propionic acid.

Calcium chloride and formic acid form a syrupy mass which, on treatment with a mixture of ether and alcohol, yields calcium chloride, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. *Calcium chloride acetate*, $\text{CaCl}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, crystallises on cooling from a solution of calcium chloride in hot glacial

acetic acid; it forms a white, hygroscopic, crystalline powder. On addition of ether to the mother liquor from the double salt, crystalline calcium chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, or, after some days, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, is precipitated.

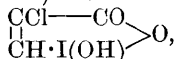
Calcium chloride propionate, $\text{CaCl}(\text{C}_3\text{H}_5\text{O}_2) \cdot \text{CaCl}_2 \cdot 2\text{C}_3\text{H}_5\text{O}_2 \cdot 4\text{H}_2\text{O}$, crystallises from the solution of calcium chloride in propionic acid in long, thin, glistening needles; if ether is added to the solution in calcium chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, which gradually changes into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, is precipitated. Strontium chloride, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, crystallises from the solution of the hexahydrate in glacial acetic acid. Anhydrous stannous chloride crystallises in needles from a solution of the dihydrate in glacial acetic acid, whilst stannic chloride dissolves in glacial acetic acid to form a colourless, non-crystallisable syrup. Some chlorides, for example, mercuric or sodium chloride, can be recrystallised from glacial acetic acid unchanged. G. Y.

Aliphatic Iodochlorides and Iodosochlorides. JOHANNES THIELE and W. PETER (*Ber.*, 1905, 38, 2842—2846).—*Chloroiodofumaric acid*, $\text{C}_4\text{H}_3\text{O}_4\text{ClI}$, formed by boiling acetylenedicarboxylic acid with iodine chloride in ethereal solution, crystallises in yellow needles, becomes brown at 180° , sinters at 200° , melts and decomposes at $226\text{--}227^\circ$, and is easily soluble in water. When treated with chlorine in ice-cooled aqueous solution, this forms the *iodosochloride*,

$\text{CO}_2\text{H} \cdot \overset{\text{Cl} \cdot \text{CO}}{\underset{\text{I}}{\text{C}}} > \text{O}$, which is obtained as a yellow, crystalline powder, sinters at 116° , melts and decomposes at $119\text{--}120^\circ$, yields free iodine when treated with potassium iodide, and is reduced by sulphurous acid to chloroiodofumaric acid. When treated with ice-cold alcohol, it is

converted into the *iodosochloride* of chloroacrylic acid, $\overset{\text{Cl} \cdot \text{CO}}{\underset{\text{I}}{\text{CH}}} > \text{O}$;

this crystallises in matted needles which become red on exposure to light, sinters and melts at $146\text{--}147^\circ$, liberates iodine from potassium iodide, and on treatment with alcohol at the laboratory temperature yields α -chloro- β -iodoacrylic acid, $\text{CHI} \cdot \text{Cl} \cdot \text{CO}_2\text{H}$. This crystallises in yellow leaflets, melts at $88\text{--}89^\circ$, and is therefore not identical with Stolz's acid (*Abstr.*, 1886, 530). *Chloroiodosoacrylic acid*,



is formed by the action of boiling water on the iodosochloride of chlorofumaric acid; it crystallises in glistening, colourless prisms, becomes yellow at 150° , softens at 173° , decomposes at 183° , and is reduced by sulphurous acid to chloroiodoacrylic acid. The *acetyl* derivative of iodosochloroacrylic acid, $\text{C}_5\text{HO}_3\text{ClI} \cdot \text{Ac}$, formed by heating the iodosochloride of chlorofumaric acid with acetic anhydride, crystallises in glistening, yellow needles, sinters at 131° , melts at $138\text{--}139^\circ$, and when treated with water yields chloroiodosoacrylic acid. Chloroiodoacrylic acid is formed when chlorofumaric iodosochloride is heated with glacial acetic acid on the water-bath.

Methyl iodochloride, $\text{Me} \cdot \text{ICl}_2$, is formed as a heavy, yellow precipitate when methyl iodide is added to a solution of chlorine in a

mixture of carbon tetrachloride and light petroleum cooled by a carbon dioxide-ether mixture. It melts at -28° , is decomposed by water with formation of methyl chloride and iodine chloride, and forms methyl iodide and free iodine with a mixture of hydriodic and hydrochloric acids at -60° , but methyl chloride at the laboratory temperature.

In the same manner, ethyl, *n*-propyl, and *n*-butyl iodides form *iodochlorides*, which are more soluble in light petroleum, and decompose with formation of iodine chlorides at lower temperatures than methyl iodochloride. *sec*-Butyl iodochloride is formed in liquid air and decomposes at -100° , below which temperature chlorine liberates iodine from *tert*-butyl iodide; allyl iodide forms an unstable *iodochloride*. *Methylene di-iodochloride* is more stable, being capable of existence for a short space of time when formed by the action of chlorine on the di-iodide in carbon tetrachloride at 0° .

With bromine in light petroleum at the laboratory temperature, iodobenzene forms an *oil* which solidifies when cooled by a mixture of carbon dioxide and ether. The action of bromine on methyl iodide in cooled light petroleum solution leads to the formation of a *substance* which crystallises in large, orange leaflets, decomposes at higher temperatures, and is probably methyl iodobromide. G. Y.

New Acids of the Oleic Series. III. Derivatives of Δ^{α} -Oleic Acid. GIACOMO PENZIO (*Atti R. Accad. Sci. Torino*, 1905, 40, 970—973. Compare Abstr., 1904, i, 548, and this vol., i, 405).— *β -Bromostearic acid*, $\text{CH}_3 \cdot [\text{CH}_2]_{14} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by the action of hydrobromic acid on 2:3-oleic acid, crystallises from light petroleum in white plates melting at 54° , and is soluble in all the ordinary organic solvents.

β -Hydroxystearic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{14} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, obtained by the action of alcoholic potassium hydroxide solution on *β -bromostearic acid*, crystallises from chloroform in white plates melting at 89° , and is soluble in alcohol or ether and to a slight extent in light petroleum. Its *sodium* salt crystallises from alcohol in white prisms. The acid described previously as *β -hydroxystearic acid*, obtained by Fremy (*Ann. Chim. Phys.*, 1837, [ii], 65, 113) and by Saytzeff (Abstr., 1887, 30), must have the hydroxyl group elsewhere than the *β -position*.

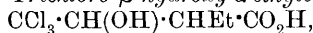
$\alpha\beta$ -Dihydroxystearic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{14} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$, prepared by oxidising Δ^{α} -oleic acid with alkaline permanganate solution, crystallises from ethyl acetate in prisms melting at 126° , and is soluble in most organic solvents and slightly so in water. The acid described by Saytzeff as *$\alpha\beta$ -dihydroxystearic acid* (Abstr., 1888, 815) must have another constitution. T. H. P.

Action of Ethyl Sodiomalonate on Ethyl Ethoxysuccinate and Ethyl Ethoxybenzylmalonate. HERMANN STAUDINGER (*Annalen*, 1905, 341, 99—117).—An attempt has been made to throw further light on the mechanism of condensations of ethyl sodiomalonate with other esters, more especially to ascertain if additive intermediate products are formed.

Ethyl malonate interacts with ethyl fumarate in alcoholic solution in the presence of 1/10 equivalent of sodium, the formation of the additive product taking place rapidly with development of heat. Ethyl ethoxysuccinate combines with ethyl malonate in the presence of one equivalent of sodium, but heat is not developed; if 1/10 equivalent of sodium is used, a very small amount of condensation takes place. In benzene solution, the addition of ethyl malonate to ethyl fumarate is complete, but there is no reaction with ethyl ethoxysuccinate. This fact demonstrates that the reaction does not depend on the formation of an additive product of sodium ethoxide with one of the reagents, for example, the ethyl malonate. Probably the ethyl sodiomalonate unites directly at the ethylene linking.

Ethyl benzylidenemalonate and ethyl ethoxybenzylmalonate were similarly compared with respect to their behaviour towards ethyl malonate in the presence of sodium ethoxide. The results obtained confirmed in every way the conclusions arrived at in the case of ethyl fumarate and ethyl ethoxysuccinate. K. J. P. O.

Ethylmalic Acid. OSCAR DOEBNER and L. SEGELITZ (*Ber.*, 1905, **38**, 2733—2737).— γ -Trichloro- β -hydroxy- α -ethylbutyric acid,



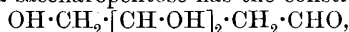
prepared by the condensation of ethylmalonic acid with chloral by means of pyridine, separates from chloroform in glistening needles and melts at 137°. The *silver*, *barium*, *calcium*, and *copper* salts were prepared. The *methyl ester* separates from methyl alcohol in stellate crystals and melts at 76°.

When γ -trichloro- β -hydroxy- α -ethylbutyric acid is warmed with a 10 per cent. aqueous solution of potassium hydroxide, potassium β -ethylmalate is formed, thus: $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CHEt} \cdot \text{CO}_2\text{H} + 5\text{KOH} = 3\text{KCl} + 3\text{H}_2\text{O} + \text{CO}_2\text{K} \cdot \text{CH}(\text{OH}) \cdot \text{CHEt} \cdot \text{CO}_2\text{K}$. β -Ethylmalic acid crystallises with difficulty but is not so hygroscopic as malic acid; it melts and decomposes at 86—87°. Its *silver*, *lead*, *copper*, and *zinc* salts are described. When β -ethylmalic acid is heated at about 200°, ethylmaleic acid is formed. A. McK.

Constitution of Meta-saccharinic Acid. HEINRICH KILIANI and PETER LOEFFLER (*Ber.*, 1905, **38**, 2667—2670. Compare Kiliani and Naegell, *Abstr.*, 1903, i, 10).—A 36 per cent. yield of pure meta-saccharopentose is obtained by distilling barium meta-saccharinate. The *phenylbenzylhydrazone*, $\text{C}_5\text{H}_{10}\text{O}_3 \cdot \text{C}_{13}\text{H}_{12}\text{N}_2$, crystallises in yellow, prismatic needles and melts at 117—118°.

On reduction with red phosphorus and concentrated hydriodic acid in a sealed tube at 140° for 7 hours, $\beta\gamma\delta$ -trihydroxyvaleric acid, formed by the action of bromine on meta-saccharopentose, yields *n*-valerolactone and a small quantity of an unsaturated acid, $\text{C}_5\text{H}_8\text{O}_3$, which forms a *calcium* salt, $\text{Ca}(\text{C}_5\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$, crystallising in stout prisms.

Meta-saccharinic acid has therefore the methylene group in the β -position and meta-saccharopentose has the constitution



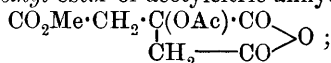
and the trihydroxyvaleric acid, $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

G. Y.

The Active Components of Fehling's Solution. FRANCIS MARRE and STOLLE (*Chem. Centr.*, 1905, ii, 615; from *Rev. gén. Chim. pure appl.*, [vii], 8, 256—258. Compare Bullnheimer and Seitz, *Abstr.*, 1899, i, 888; 1900, i, 330).—If in preparing Fehling's solution the copper sulphate is replaced by the calculated amount of copper hydroxide and the salts dissolved in as little warm water as possible, there separates out the substance $C_8H_4O_{12}CuNa_4K_2 \cdot H_2O$, which is the active component of Fehling's solution. It may have the constitution $Cu[O \cdot CH(CO_2Na) \cdot CH(OK) \cdot CO_2Na]_2$ or $Cu[O \cdot CH(CO_2Na) \cdot CH(ONa) \cdot CO_2K]_2$. G. Y.

Symmetrical Dialkyl Esters of Citric Acid. GEORG SCHROETER (*Ber.*, 1905, 38, 3190—3201. Compare Schroeter and Schmitz, *Abstr.*, 1902, i, 531).—[With LEONHARD SCHMITZ.]—*Methyl dihydrogen citrate*, $CO_2H \cdot CH_2 \cdot C(OH)(CO_2H) \cdot CH_2 \cdot CO_2Me$, is obtained from the mother liquors from the preparation of *s*-dimethyl hydrogen citrate (*loc. cit.*); it crystallises from glacial acetic acid or acetone and melts at 166—167°.

s-Dimethyl hydrogen acetylcitrate, $OAc \cdot C(CH_2 \cdot CO_2Me)_2 \cdot CO_2H$, formed by the action of acetic anhydride and concentrated sulphuric acid on the dimethyl ester, separates from a mixture of chloroform and light petroleum in nodular crystals, melts at 75°, and is easily soluble in water, alcohol, ether, chloroform, or ethyl acetate. When boiled with absolute methyl alcohol, acetylcitric anhydride forms *methyl dihydrogen acetylcitrate*, $CO_2Me \cdot CH_2 \cdot C(OAc)(CO_2H) \cdot CH_2 \cdot CO_2H$, which is obtained as a syrup, and is converted by boiling acetyl chloride into the *methyl* ester of acetylcitric anhydride,



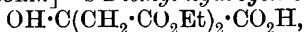
this crystallises in white needles, melts at 108—110°, and when warmed with methyl alcohol yields *s*-dimethyl hydrogen acetylcitrate, which reacts with phosphorus pentachloride to form the *chloride*, $OAc \cdot C(CH_2 \cdot CO_2Me)_2 \cdot COCl$, as a yellow oil. Owing to its instability towards moisture and heat, this could not be obtained in a state of purity; when treated with anhydrous ammonia in chloroform solution, it forms the *amide*, $OAc \cdot C(CH_2 \cdot CO_2Me)_2 \cdot CO \cdot NH_2$, which separates from a mixture of chloroform and ether in prismatic crystals, melts at 108—109°, and is easily soluble in water and most organic solvents, but is only sparingly so in ether or light petroleum.

[With R. SCHWAMBORN.]—When warmed with sulphuric acid, *s*-dimethyl hydrogen citrate decomposes with evolution of carbon monoxide and formation of acetonedicarboxylic acid.

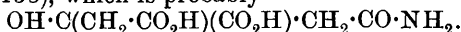
[With LEONHARD SCHMITZ.]—The *nitrile*, $CN \cdot C(OH)(CH_2 \cdot CO_2Me)_2$, is formed when the calculated amount of fuming hydrochloric acid is added to a mixture of potassium cyanide and dimethyl acetonedicarboxylate in ethereal solution; it crystallises from water or chloroform, melts at 53°, and when dissolved in cold concentrated sulphuric acid is hydrolysed to the *amide*, $NH_2 \cdot CO \cdot C(OH)(CH_2 \cdot CO_2Me)_2$, which crystallises from a mixture of chloroform and light petroleum and melts at 106—107°. This dissolves without change in cold concentrated sulphuric acid or in acetic anhydride, but is converted by

acetyl chloride into a *substance* which has C=47.21, H=5.78, N=5.03 per cent., crystallises from hot water, and melts at 103—104°. When carefully treated with the calculated amount of sodium nitrite in strongly cooled concentrated sulphuric acid solution, the amide is converted into *s*-dimethyl hydrogen citrate melting at 125—126°.

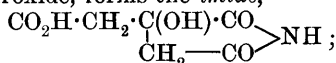
[With R. SCHWAMBORN.]—*s*-Diethyl hydrogen citrate,



is prepared by boiling citric acid with absolute alcohol and a small amount of concentrated sulphuric acid; the ester is isolated as the calcium salt; it is an oil which is easily soluble in water, and can be extracted from its aqueous solution by means of ether. The *silver* salt, $\text{C}_{10}\text{H}_{15}\text{O}_7\text{Ag}$, crystallised in voluminous, slender leaflets. The *amide*, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2\cdot\text{CO}\cdot\text{NH}_2$, can be prepared by the action of potassium cyanide and hydrochloric acid on ethyl acetonedicarboxylate and hydrolysis of the *nitrile* so obtained by means of cold concentrated sulphuric acid; it crystallises from a mixture of chloroform and light petroleum in slender, white needles, and sinters and melts at 74°. On hydrolysis with aqueous sodium hydroxide, it yields *citramonamic acid*, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{CO}\cdot\text{NH}_2$, which forms a *silver* salt, $\text{C}_6\text{H}_7\text{O}_6\text{NAg}_2$, crystallising in slender, white needles, and is not identical with Behrmann and Hofmann's acid (Abstr., 1885, 138), which is probably



When distilled under 13 mm. pressure, the ester-amide yields alcohol and a *substance* which distils at 180—230°, and, on hydrolysis with aqueous sodium hydroxide, forms the *imide*,



this forms a *silver* salt, $\text{C}_6\text{H}_6\text{O}_5\text{NAg}, \text{AgNO}_3$. When heated with phenylcarbimide in benzene solution, the ester-amide forms the *phenyl-urethane*, $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2\cdot\text{CO}\cdot\text{NH}_2$, which crystallises from alcohol and melts and decomposes at 146°.

The ester-amide interacts with benzoyl chloride at 130° to form the

benzoyl derivative, $\text{OBz}\cdot\underset{\text{CH}_2-}{\overset{\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}}{\text{C}}}>\text{NH}$, which crystallises

in needles, melts at 115°, and when treated with 2*N*-sodium hydroxide forms a blood-red solution which rapidly becomes colourless and, on addition of the calculated quantity of hydrochloric acid, yields benzoic acid, and, on a further addition of hydrochloric acid and cooling to 0°, the *as*-imide of aconitic acid melting at 191° (this vol., i, 819).

G. Y.

Dihydroxypropanetricarboxylic and $\alpha\gamma$ -Dihydroxyglutaric Acids. HEINRICH KILIANI and F. HEROLD (*Ber.*, 1905, **38**, 2671—2676. Compare Kiliani, Abstr., 1885, 744; 1886, 48; Ruff and Meusser, Abstr., 1902, i, 591).— $\alpha\gamma$ -Dihydroxypropane- $\alpha\alpha\gamma$ -tricarboxylic acid is prepared best by warming calcium *isosaccharinate* with concentrated nitric acid at 35° and finally at 45—50°. After removal of the calcium oxalate, the product is evaporated with sufficient calcium carbonate to form the normal salt, which is dissolved in water

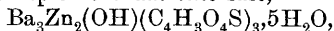
and converted into the acid salt by precipitation of two-thirds of the calcium with oxalic acid. The filtrate, after concentration, slowly deposits the acid calcium salt of the lactone, $(C_6H_5O_7)_2Ca, 2H_2O$ or $5H_2O$, which crystallises in thin prisms, and loses water and commences to decompose at $100-120^\circ$. The tricarboxylic acid is obtained, on evaporation of its solution in a vacuum, as a viscid syrup, which crystallises in deliquescent plates and prisms. The *copper* salt, $(C_6H_5O_8)_2Cu_3$, is light blue; the *quinine* salt, $C_6H_8O_8, 3C_{20}H_{24}O_2N_2, 3H_2O$, crystallises in sheaves of needles and melts at 142° .

α -Dihydroxyglutaric acid is obtained in the form of its *lactone*, $(C_5H_6O_5)_2, H_2O$, which melts at $164-165^\circ$, by boiling the acid calcium salt just mentioned with the calculated amount of aqueous oxalic acid, evaporating the filtrate in a vacuum, and washing the crystalline residue with a small amount of water.

α -Dihydroxyglutaric acid, free from its lactone, is obtained by treating its calcium salt with oxalic acid and evaporating the filtrate over sulphuric acid in a vacuum; it crystallises in colourless plates or prisms, commences to soften at 115° , and melts above 120° . The *zinc*, $2C_5H_6O_6Zn, 3H_2O$, and the *copper*, $C_5H_6O_6Cu, H_2O$, salts are described.

G. Y.

Formation of Complex Salts with Thio-acids. II. Thiomalic Acids and their Salts. ARTHUR ROSENHEIM and WILHELM STADLER (*Ber.*, 1905, **38**, 2687—2690. Compare Rosenheim and Davidsohn, *Abstr.*, 1904, i, 843; Büllmann, this vol., i, 625).—Thiomalic acid melts at 150° and has the molecular conductivity $\mu = 46.0$ with $v = 32$ or $\mu = 251.2$ with $v = 2048$ at 25° , and the affinity constant $K = 0.0523$. It forms an alcoholic or aqueous solution, neutral to phenolphthalein, on addition of 2 mols. of sodium hydroxide, and for oxidation requires about five equivalents of iodine, as also more potassium permanganate than is necessary for its conversion into dithiodimalic acid. The *ethyl* ester, $CO_2Et \cdot CH(SH) \cdot CH_2 \cdot CO_2Et$, is an oil which boils with partial decomposition at 246° ; the *benzyl* ester boils and decomposes at $250-280^\circ$. The *mono-sodium*, $C_4H_5O_4SNa, \frac{1}{2}H_2O$, and *mono-ammonium* salts are crystalline; the *di-alkali* salts form vitreous masses; the crystalline *di-barium*, $C_4H_4O_4SBa, \frac{1}{2}H_2O$, and *dizinc* salts are described; the *tri-alkali thiolmalates* form amorphous, flocculent precipitates. Sodium thiolmalate in neutral aqueous solution gives with cobalt carbonate a brownish-red, with bismuth carbonate a yellow, coloration. On dissolving zinc carbonate in aqueous dipotassium thiolmalate and evaporating the solution, an amorphous, hygroscopic mass is obtained; with barium chloride in aqueous solution, this forms a complex *barium zinc* salt,



which is obtained as a flocculent, white precipitate.

G. Y.

Formaldehyde and Formate Formation. FRIEDRICH AUERBACH (*Ber.*, 1905, **38**, 2833—2836).—A criticism of Euler and Euler's paper (this vol., i, 633).

G. Y.

Action of Acetaldehyde and Acetone on Mercuric Acetate. A. LASSERRE (*J. Pharm. Chim.*, 1905, [vi], **22**, 246—249).—A cold

aqueous solution of mercuric acetate is reduced by the action of aliphatic aldehydes, paraldehyde, acetals, or aldoses, mercurous acetate crystallising from the solution after some hours. The aliphatic alcohols, acetone, or the ketoses have no such reducing action. The compound CMeHO, HgO , obtained by the addition of sodium hydroxide to a solution of mercuric acetate and acetaldehyde at 0° , is a pale yellow powder, deflagrating at 180° , soluble in solutions of mercuric acetate, potassium iodide, sodium thiosulphate, or hydrogen sulphite, and insoluble in water, sulphuric, acetic, tartaric, or oxalic acid or in the ordinary organic solvents (compare Leys, this vol., ii, 655). The compound $\text{COMe}_2, 2\text{HgO}$, obtained by warming an alkaline solution of mercuric acetate and acetone, is a yellow powder, insoluble in water and yielding acetone on distillation with dilute phosphoric acid; the compound $(\text{COMeEt})_2, 3\text{HgO}$ is similarly obtained from methyl ethyl ketone (compare Reynolds, Abstr., 1871, 561). M. A. W.

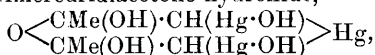
Action of Bases on Chloral Hydrate. JOHANNES E. ENKLAAR (*Rec. Trav. chim.*, 1905, [ii], 24, 419—444. Compare Werner, Trans., 1904, 85, 1376, and Böttger and Kötze, Abstr., 1902, i, 659).—The results of further experiments on the velocity of decomposition of chloral hydrate by calcium hydroxide in the presence of neutral salts serve to show that the second explanation of the mechanism of the reaction already suggested by the author (compare this vol., i, 170) is the correct one, namely, the salt of chloral hydrate which is first formed is highly dissociated in solution, and the complex negative ion breaks down into chloroform and the negative ion of formic acid, according to the equations $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2 + \text{KOH} \rightleftharpoons \text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{OK} + \text{H}_2\text{O}$; $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{OK} \rightleftharpoons \text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{O}^- + \text{K}^+$; $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{O}^- = \text{CHCl}_3 + \text{CHO} \cdot \text{O}^-$. That chloral hydrate is a feeble acid and therefore capable of forming salts is shown by the fact that it has a specific conductivity of 6.57 to 5.73×10^{-6} in $N/100$ solution at 0.65° , the corresponding values for calcium formate and calcium hydroxide being 522.9×10^{-6} and 1372×10^{-6} respectively, the conductivity of water being 2.5 to 2.4×10^{-6} . M. A. W.

Transformations of the Isomeric Trithioaldehydes. J. F. SUYVER (*Rec. Trav. chim.*, 1905, [ii], 24, 377—403. Compare Baumann and Fromm, Abstr., 1891, 1010).— α -Trithioaldehyde (m. p. 100 — 101°) is not transformed into the β -isomeride (m. p. 125 — 126°) by the action of heat, for it is unchanged after heating at 140° for 24 hours, but certain catalytic agents, such as hydrogen chloride, iodine, zinc chloride, acetyl chloride, ethyl iodide, Beckmann's mixture, or sulphur trioxide or sulphonyl chloride dissolved in chloroform, acting on the substance either fused or in solution, convert it into the β -isomeride to the extent of from 89 to 98 per cent., and the reaction is a balanced one, for β -trithioaldehyde is transformed into the α -isomeride to the extent of from 11 to 2 per cent. under similar conditions. It was not possible to separate the two isomerides in the equilibrium mixtures by the action of solvents, as the solubility of each compound in the ordinary organic solvents is the same; the composition of the mixtures

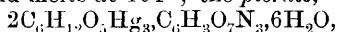
was therefore determined by comparing their solidifying points with those of mixtures containing known proportions of the two isomerides. α -Trithiobenzaldehyde (m. p. 166—167°) is converted into the β -isomeride (m. p. 225—226°) to a small extent on heating, to the extent of 2.9 per cent. on boiling in benzene solution at 81°, or to 17.4 per cent. in toluene at 111°; such catalytic agents as acetyl chloride, hydrogen chloride in alcoholic solution, or sulphur trioxide or iodine in chloroform solution completely convert the α -compound into the β -isomeride; whilst Beckmann's mixture, or a solution of iodine in carbon bisulphide, toluene, or benzene, effects a partial conversion. The transformation of α -trithiobenzaldehyde into the β -isomeride is not a reversible reaction, and the relative proportion of the two isomerides in the final mixtures is determined by extraction with benzene, in which solvent the α -isomeride is soluble to the extent of 6.08 parts in 100 parts of solvent at 25°, whilst the β -isomeride is practically insoluble. M. A. W.

Ketone and Aldehyde Reactions. PAVEL IW. PETRENKO-KRITSCHENKO [with EUGEN ELTSCHANINOFF, E. KESTNER and TH. DOLGOPOLOFF] (*Annalen*, 1905, **341**, 150—171).—The velocity of the reaction of various aliphatic, aromatic, and cyclic saturated ketones and aldehydes with phenylhydrazine and potassium hydrogen sulphite has been measured. The results have been previously published (*Abstr.*, 1903, i, 440, and this vol., i, 354). K. J. P. O.

Compounds of Ketones and Aldehydes with Mercuric Oxide. S. M. AULD and ARTHUR HANTZSCH (*Ber.*, 1905, **38**, 2677—2685).—Trimercuridiacetone hydroxide,



is formed by the action of freshly precipitated mercuric oxide on acetone in aqueous solution in presence of baryta (compare Reynolds, this *Journal*, 1871, **24**, 561). The baryta is precipitated by means of carbon dioxide, the excess of the latter removed by a current of air, and the filtrate evaporated, when the product is obtained as a sticky syrup, which dissolves in much water, forming a clear, almost colourless solution. This has a slight alkaline reaction and the electrical conductivity $\mu = 0.018$ with $v = 256$ or $\mu = 0.022$ with $v = 512$ at 18°. The haloid salts are formed by carefully adding hydrogen haloids to the aqueous solution of the hydroxide. The *dichloride*, $\text{C}_6\text{H}_{10}\text{O}_2\text{Hg}_3\text{Cl}_2$, forms a colourless powder, which becomes yellow when heated, melts at about 110°, is easily soluble in pyridine or aniline, but only sparingly so in alcohol, and is almost insoluble in water; the *platinichloride*, $\text{C}_6\text{H}_{10}\text{O}_3\text{Hg}_3\text{PtCl}_6$, forms an amorphous, brown precipitate and detonates at 178°; the *tribromide* crystallises in small, white needles and melts at 127°; the *di-iodide*, formed by the action of cold acetic acid on a mixture of the hydroxide and potassium iodide, crystallises in small needles and melts at 104°; the *picrate*,

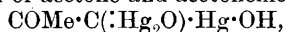


forms small, yellow crystals, is easily soluble in hot water, and has the

electrical conductivity $\mu = 0.042$ with $\nu = 1100$ at 25° . On adding concentrated hydrogen haloids or strong oxy-acids to the hydroxide, immediate decomposition to acetone and the mercuric salt takes place, but if a slight excess of hydrochloric acid having $\nu = 40$ is added to a solution of the base with $\nu = 512$, the reaction takes place more slowly, and the solution has the electrical conductivities $\mu = 0.00213$, 0.00214 , 0.00200 , 0.00195 , 0.00191 , and 0.00187 respectively 1, 3, 6, 8, 12, and 25 minutes after mixing.

The action of bromine in potassium bromide solution on the aqueous solution of the base leads to the formation of mercuric dibromide and *as*-dibromoacetone, which, on prolonged shaking of the mixture, is converted into methylglyoxime.

Reynolds' insoluble polymeride of trimercuridiacetone hydroxide (*loc. cit.*) is formed by the action of alkali hydroxides or, more slowly, of salts or of sunlight on the aqueous solution of the base. The action of boiling aqueous alkali hydroxides on the base or its polymeride leads to the formation of acetone and acetonecarbidide,



which is identical with Hofmann's compound (Abstr., 1898, i, 635). Acetophenone and mercuric oxide interact only on prolonged digestion at 100° to form a yellow, insoluble *product* which, on treatment with hydrochloric acid, yields acetophenone and mercuric chloride.

The action of mercuric oxide on acetaldehyde in slightly alkaline solution leads to the formation of a colourless solution which probably contains trimercuridialdehyde hydroxide, as it is indifferent towards phenylhydrazine, hydroxylamine, or rosaniline decolorised by sulphurous acid. The base cannot be isolated, as it changes more easily than the acetone compound into the *polymeride*, $(\text{C}_4\text{H}_8\text{O}_5\text{Hg}_3)_x$, which is formed immediately as a white powder by warming a dilute solution of acetaldehyde with a solution of mercuric chloride made alkaline with potassium hydroxide. This may be used as a test to detect the presence of small quantities of acetaldehyde (1 in 6000 aq.). The polymeride decomposes without melting at about 100° , is practically insoluble in all organic solvents, and is decomposed by hydrochloric acid, but not by dilute acetic acid, with formation of acetaldehyde and mercuric chloride.

G. Y.

Complex Compounds of α -Dioximes. LEO TSCHUGAEFF (*Zeit. anorg. Chem.*, 1905, 46, 144—169).—The α -dioximes differ from all others in reacting with nickel, cobalt, iron, platinum, palladium, and copper salts to form stable salts, called by the author *dioximines*.

The nickel derivative of dimethylglyoxime, *nickel dimethylglyoximine*, $(\text{CMe:NO})\text{Ni}(\text{CMe:NOH})$, is obtained as a scarlet, crystalline precipitate on adding a hot saturated alcoholic solution of dimethylglyoxime to one of nickel acetate. It is almost insoluble in water, slightly soluble in alcohol, ether, benzene, glacial acetic acid, or pyridine. It can be sublimed undecomposed and is very stable towards most reagents. Alkali hydroxides and ammonia, alkali and ammonium carbonates, and hydrogen sulphide do not attack it; ammonium

sulphide acts only slowly. Weak acids have no action, but with strong acids the reversible reaction, $C_8H_{14}O_4N_4Ni + 2HX \rightleftharpoons 2C_4H_8O_2N_2 + NiX_2$, takes place. The remaining glyoximines described closely resemble the nickel compound.

Nickel methylethylglyoximine, $C_{10}H_{18}O_4N_4Ni$, forms brownish-red, prismatic crystals and melts at about 280° . *Nickel methylpropylglyoximine*, $C_{12}H_{22}O_4N_4Ni$, is obtained by digesting nickel acetate with the oxime in aqueous alcoholic solution. It forms orange-red crystals and melts at about 144° . It is even more soluble than the preceding compounds in organic solvents; the solution in benzene shows a freezing point corresponding with the above molecular weight. *Nickel methylisobutylglyoximine*, $C_{14}H_{26}O_4N_4Ni$, forms orange-red needles and melts at 160° . *Nickel diphenylglyoximine*, $C_{24}H_{22}O_4N_4Ni$, formed from nickel acetate and α -benzildioxime, melts and decomposes at 300° . *Nickel ditolylglyoximine*, $C_{32}H_{30}O_4N_4Ni$, is somewhat more soluble than diphenylglyoximine in organic solvents; it forms brownish-red prisms. *Nickel carbethoxymethylglyoximine*, $C_{12}H_{18}O_8N_4Ni$, forms dark brownish-violet needles, melts at $202.5-203.5^\circ$, is fairly soluble in organic solvents, and sublimes when heated in a vacuum. It is more easily attacked by reagents than the remaining glyoximines.

The platinoglyoximines are all crystalline, closely resemble the nickel glyoximines, and are formed by adding a boiling acetic acid solution of the glyoxime to a boiling aqueous solution of potassium platinochloride or platinum-*cis*-dichlorodipyridine, and after addition of ammonium acetate digesting for a time on the water-bath. The platinodioximines are even more stable than the nickel compounds; as in the case of the latter, potassium cyanide appears to be the only reagent which easily and completely decomposes them with separation of free dioxime. They are soluble in dilute alkalis and take up bromine to form dibromides. In a vacuum they can be sublimed without decomposition.

Platinomethylethylglyoximine, $C_{10}H_{18}O_4N_4Pt$, forms dark brown needles. *Platinomethylethylglyoximine bromide*, $C_{10}H_{18}O_4N_4PtBr_2$, is formed when bromine is added to the preceding compound in chloroform solution. It separates as a brown, crystalline powder, moderately soluble in most organic solvents, very slightly soluble in water. It is very stable towards acids, but is reduced by hydrogen sulphide. *Platinomethylpropylglyoximine*, $C_{12}H_{22}O_4N_4Pt$, has a normal molecular weight in benzene solution, and forms brown needles which melt at 252° .

Platinomethylisobutylglyoximine, $C_{14}H_{26}O_4N_4Pt$, melts at about 220° . *Platinodiphenylglyoximine*, $C_{28}H_{22}O_4N_4Pt$, is best obtained by digesting platinum-*cis*-dichlorodipyridine with α -benzildioxime in aqueous acetic acid solution. It forms reddish-brown needles which are decomposed by heating to a high temperature, are only very slightly volatile even in a vacuum, and dissolve very sparingly in organic solvents.

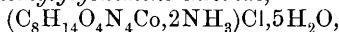
Palladomethylethylglyoximine, $C_{10}H_{18}O_4N_4Pd$, prepared from palladium ammonium chloride and methylethylglyoxime, forms canary-yellow needles which melt and decompose at about 290° but can be sublimed unchanged in a vacuum. *Palladomethylpropylglyoximine*,

$C_{12}H_{22}O_4N_4Pd$, melts at $176-177^\circ$. *Palladodiphenylglyoximine*, prepared by adding a concentrated aqueous solution of palladium ammonium chloride to a solution of α -benzildioxime in pyridine, has not been further examined.

Cupric dimethylglyoximine, $C_8H_{14}O_4N_4Cu$, forms dark crystals which are soluble in water and most other solvents to dark brown solutions. It decomposes on heating at 200° , and cannot be sublimed in a vacuum without decomposition. It is less stable towards reagents than the corresponding nickel, platinum, and palladium compounds.

Bivalent iron does not appear to form simple compounds like those given by the preceding four metals. Complex compounds are easily obtained which contain the dioxime group in combination with bases like pyridine. A number of these have been prepared qualitatively from α -dioximes which contain both hydroxyls in the *cis*-position. *Ferrodipyrindinemethylglyoximine*, $C_{20}H_{28}O_4N_4Fe$, prepared by the action of a concentrated aqueous solution of ferrous sulphate on an alcoholic solution of methylethylglyoxime to which excess of pyridine has been added, forms brownish-red, dichroic prisms easily soluble in pyridine, more sparingly in alcohol, chloroform, or benzene, scarcely at all in water.

Cobaltous dioximines have not yet been prepared in a pure condition, but strongly basic complex cobaltic dioximines, which contain besides the dioximine group also ammonia or other base, are easily obtained. *Cobaltodiamminedimethylglyoximine chloride*,



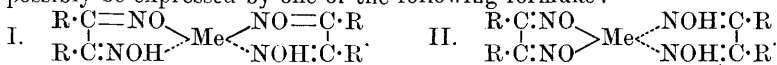
is formed by the action of roseopentamminecobaltic chloride or purpureocobaltic chloride on dimethylglyoximine. The electrical conductivity shows that the compound must be grouped with the tetramine bases of the general formula $(Co, 4ClX_2)X'$. It forms yellowish brown crystals easily soluble in hot water, very sparingly soluble in alcohol or ether.

The *base* $(C_8H_{14}O_4N_4Co, 2NH_3)OH$ is obtained in solution by the action of silver hydroxide on a concentrated solution of the hydrochloride. It is strongly alkaline. The *nitrate*, $C_8H_{20}O_7N_7Co$, formed by interaction of the hydrochloride and sodium nitrate, crystallises in anhydrous, yellow needles. The *sulphate*, $[C_8H_{20}O_4N_6Co]_2SO_4$, forms thick, microscopic, yellow tablets; according to molecular weight and conductivity experiments, it dissociates into three ions.

A comparison of, for instance, a platinodioximine with Peyrone's salt, $Pt, 2NH_3Cl_2$, shows that in the dioximine the two NO groups correspond with the two chlorine atoms, and the two NOH groups with the two ammonia molecules. The two NO groups play the part of a dibasic acid, and the two NOH groups the rôle of a diacid base. According to Werner's theory, the NO groups are to be regarded as attached to the platinum by major, the NOH groups by minor, valencies: $\begin{array}{c} :NO > \\ :NO > \end{array} Pt \begin{array}{c} < NOH: \\ < NOH: \end{array}$. Similar expressions may be used for the

dioximines of the other metals mentioned above. The dibromide, $C_8H_{18}O_4N_4Br_2Pt$, which appears to be analogous with Gerhardt and Cleve's compounds $(Pt, 2NH_3X_4)$, may be deduced in corresponding manner from the quadrivalent platinum atom with the co-ordination number six.

If it is assumed that in the dioximine molecule not only the NO but also the NOH residue is in direct union with the metal, then the assumption must also be made that in these compounds cyclic atomic unions are present. Thus the construction of the dioximines may possibly be expressed by one of the following formulæ:



The stability of the dioximines is consistent with a cyclic formula.

D. H. J.

Formation of Isodynamic Glucosides with reference to the Theory of Isomeric Change and the Selective Action of Enzymes. Preparation of β -Methylglucoside. E. FRANKLAND ARMSTRONG and S. L. COURTAULD (*Proc. Physiol. Soc.*, 1905, iv; *J. Physiol.*, 33).—Use is constantly made of the stereoisomeric glucosides as test materials in studying enzyme action, and it is important to be able to prepare them easily. The following method renders β -methyl glucoside readily obtainable. When solid anhydrous α -glucose is dissolved in dry methyl alcohol containing dry gaseous hydrogen chloride, it is rapidly changed into a mixture of nearly equal parts of α - and β -glucose, which then undergo etherification, yielding a mixture of the two glucosides in nearly equal amounts. If the solution is neutralised before the further slow conversion of the β -methyl glucoside into the more stable α -isomeride can take place, and the solvent is removed, a mixture of the two glucosides is obtained. The α -glucoside is then best destroyed by fermenting it with Hansen's *Saccharomyces intermedians*, and the pure β -compound is left. Of this, 230 grams can be obtained from 500 of dextrose. The α -isomeride is best prepared by Fischer's method, namely, by using less acid and heating until an equilibrated mixture of the two glucosides is obtained; this contains 77 per cent. of the α -compound. After the greater part of this has crystallised out, the mother liquors may again be heated so as to convert part of the β -glucoside into the α -form; this may finally be purified from traces of the β -compound by treatment with emulsin.

W. D. H.

Fucosephenylosazone. W. MAYER and BERNHARD TOLLENS (*Ber.*, 1905, 38, 3021—3022. Compare Müther and Tollens, *Abstr.*, 1904, i, 226).—Pure fucosephenylosazone melts at 177.5°, and is undoubtedly the antipodal isomeride of rhodosephenylosazone. It is best prepared by Votoček's method (*Abstr.*, 1904, i, 975), the mixture being heated for 1½ hours. The products of low melting point described previously were mixtures of hydrazone and osazone.

J. J. S.

Cellulose. HANS RIESENFELD and F. TAURKE (*Ber.*, 1905, 38, 2798—2800).—A specimen of wood cellulose was insoluble in Schweizer's reagent, but dissolved in an ammoniacal solution of cupric carbonate. Salts, acids, water, or alcohol yielded precipitates with the solution. Metallic zinc, cadmium, aluminium, and lead completely precipitated the cellulose as well as the copper, whereas iron, nickel, and tin were without action.

When heated, the solution produced a brownish-black precipitate, containing about 56 per cent. of copper and 23–26 per cent. of cellulose.

J. J. S.

Mutual Solubilities of Diethylamine and Water. ROBERT TABOR LATTEY (*Phil. Mag.*, 1905, [vi], 10, 397–399. Compare Guthrie, *Abstr.*, 1885, 339).—Diethylamine and water form a pair of liquids which are completely miscible below a certain temperature, above which they become partially miscible. In the following table the temperatures of separation of various mixtures are given :

Per cent. amine	21·73	22·65	25·04	25·06	28·60	30·93	34·03	38·18
Temperature of separation.	154·5°	151·7°	147·5°	147·0°	144·4°	144·0°	143·2°	143·5°

Per cent. amine	39·63	45·78	48·89	51·71	54·24	54·78	58·59	58·99
Temperature of separation.	143·5°	144·15°	145·0°	146·8°	148·5°	150·3°	152·3°	156·0°

The critical temperature is 143·5° and the critical concentration of the amine 37·4 per cent., whereas the older experiments of Guthrie give 121° and 19 per cent.

It was found that trustworthy data could only be obtained when the liquids were heated in Jena glass tubes, and the inaccuracy of Guthrie's observations is attributable to the solvent action of the liquid on the glass of the apparatus used.

H. M. D.

Constitution of Ammonium Salts. JOHN C. CAIN (*Ber.*, 1905, 38, 2715–2716).—The author discusses the reactions of dibromides of tertiary amines (compare Hantzsch, this vol., i, 576), the action of hypochlorous acid on trimethylamine, and the action of hydrogen chloride on trimethylamine oxide, from the standpoint of the theory of ammonium salts formerly advanced by him (*Abstr.*, 1904, ii, 726).

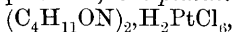
A. McK.

Supposed Isomerism of Tetramethylammonium Iodide Mercuricyanide. S. M. AULD and ARTHUR HANTZSCH (*Ber.*, 1905, 38, 2685–2686).—Contrary to the statement of Claus and Merck (*Abstr.*, 1884, 338), only one, the white, tetramethylammonium iodide mercuricyanide is formed by the action of mercuric cyanide on tetramethylammonium iodide in aqueous solution. If these salts are allowed to interact in dilute acetic acid solution and the product boiled with water, hydrogen cyanide is evolved and two salts are formed : the one, $2\text{NMe}_4\text{I}, 3\text{HgI}_2, \text{HgI}\cdot\text{OH}$, crystallises from acetone in large, deep yellow prisms, melts at 187–188°, and is almost insoluble in water. The second, $2\text{NMe}_4\text{I}, \text{HgI}_2, \text{HgI}\cdot\text{OH}$, forms small, yellow crystals, melts at 246°, is slightly soluble in water, and easily decomposes with formation of mercuric iodide.

G. Y.

Aminoethyl Ether. LUDWIG KNORR and GEORG MEYER (*Ber.*, 1905, 38, 3129–3136. Compare Knorr, *Abstr.*, 1904, i, 854, 916, 938).—Aminoethyl ether has the sp. gr. 0·8512 at 20°/4°, n_D 1·4101 at 20°, and m_{Na} 25·76. The *picrolonate*, $\text{C}_4\text{H}_{11}\text{ON}, \text{C}_{10}\text{H}_8\text{O}_5\text{N}_4$, crystallises in stout, yellow prisms and melts and decomposes at 204°; the *picrate*, $\text{C}_4\text{H}_{11}\text{ON}, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, forms stout, yellow crystals, and sinters and melts

at 122° ; the *hydrochloride*, $C_4H_{11}ON, HCl$, crystallises in shimmering, white leaflets and is deliquescent; the *platinichloride*,



crystallises in long, hair-like needles and melts and decomposes at 192° . The *carbamide*, $NH_2 \cdot CO \cdot NH \cdot C_2H_4 \cdot OEt$, forms an oil which solidifies to a crystalline, colourless mass when cooled and stirred with ether; it sinters at 53° , melts at 56° , and is very soluble in water or alcohol. The *phenylcarbamide*, $NHPh \cdot CO \cdot NH \cdot C_2H_4 \cdot OEt$, crystallises from a mixture of benzene and light petroleum in white needles and melts at $68-70^{\circ}$. The *phenylthiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_2H_4 \cdot OEt$, crystallises from alcohol in white needles and melts at 112° .

Aminoethyl ether interacts with acetylacetone with development of heat and formation of the *anhydride*, $C_9H_{17}O_2N$, which forms a yellow oil possessing a fruity odour and boiling at 254° under 752 mm. pressure. With acetonylacetone, aminoethyl ether interacts to form the *pyrrole*

derivative, $\begin{matrix} CH:CM \\ CH:CM \end{matrix} > N \cdot C_2H_4 \cdot OEt$, which is obtained as a yellow oil,

boiling at $225-226^{\circ}$ under 751 mm. pressure and giving the pine-wood reaction.

Methylchloroethylamine hydrochloride (Marckwald and Frobenius, Abstr., 1902, i, 23) can be prepared by heating methylaminoethyl alcohol with fuming hydrochloric acid at $160-170^{\circ}$; the *aurichloride*, $C_3H_8NCl, HAuCl_4$, crystallises in yellow needles and melts at 126° ; the *bismuthiodide* crystallises in purple, hexagonal prisms and melts at 208° .

Methylbromoethylamine hydrobromide, prepared by heating methylaminoethyl alcohol with hydrobromic acid of sp. gr. 1.49 at 160° , crystallises from alcohol and sinters and melts at about 80° (compare Marckwald, loc. cit.).

Methylaminoethyl ether, $NHMe \cdot CH_2 \cdot CH_2 \cdot OEt$, is formed along with methylethylenimine and dimethylpiperazine by the action of alcoholic sodium ethoxide on methylechloroethylamine hydrochloride or methylbromoethylamine hydrobromide at 160° , or alone by the action of absolute alcohol on the amine salts at 160° . It is obtained as a mobile liquid, which boils at $114-115^{\circ}$ under 744 mm. pressure and has the sp. gr. 0.8363 at $20^{\circ}/4^{\circ}$, n_D 1.4147, and m_{Na} 30.82. It has an amine-like odour and an alkaline reaction, and is miscible in all proportions with water, alcohol, or ether. The salts are easily soluble, and crystallise only from concentrated solutions; the *aurichloride*, $C_5H_{13}ON, HAuCl_4$, crystallises in long, yellow needles and melts at 127° ; the *platinichloride*, $(C_5H_{13}ON)_2, H_2PtCl_6$, forms needles and melts and decomposes at 208° ; the *picrate*, $C_5H_{13}ON, C_6H_3O_7N_3$, crystallises in concentric aggregates of prisms and melts at 119° ; the *picrotonate*, $C_5H_{13}ON, C_{10}H_8O_5N_4$, crystallises in yellow needles, blackens at 109° , and melts at 111° . The *phenylthiocarbamide*, $NHPh \cdot CS \cdot NMe \cdot CH_2 \cdot CH_2 \cdot OEt$, separates from alcohol in brown crystals and melts at $78-80^{\circ}$.

A table is given showing the melting points, sp. gr., and refractive indexes of amino-, methylamino-, and dimethylamino-ethyl alcohol and of the three corresponding ethers.

G. Y.

Metastable States in Reactions between Gaseous and Solid Substances. HEINRICH LEY and G. WIEGNER (*Zeit. Elektrochem.*, 1905, 11, 585—593).—When copper aminoacetate is exposed to dry ammonia gas, it takes up two molecules of ammonia. The compound has a dissociation pressure of less than 100 mm. at the ordinary temperature, notwithstanding which the combination of the copper aminoacetate with ammonia at atmospheric pressure takes place at first extremely slowly; after a considerable period of induction, the reaction starts suddenly, and then goes on with constant velocity until it is complete. The length of the initial period depends on the dryness of the salt; a trace of moisture (other than water of crystallisation) diminishes the initial period very considerably; for example, the reaction began after 63 hours with a very carefully dried sample, whilst with another containing water of crystallisation it began in six minutes. During the initial period, nuclei of the ammonia compound appear to be formed; these can sometimes be seen owing to the difference in colour. T. E.

Synthesis of Amino-acids. V. α -Amino- δ -hydroxyvaleric Acid. S. P. L. SÖRENSEN (*Chem. Centr.*, 1905, ii, 398—401; from *Compt. rend. trav. Labor. Carlsberg, Copenhagen*, 1905, 6, 137—192. Compare Abstr., 1903, i, 833).—Ethyl sodiophthaliminomalonate, on treatment with trimethylene dibromide, gives *ethyl γ -bromopropylphthaliminomalonate*, $\text{C}_3\text{H}_6\text{Br}\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{N}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$; from this, the corresponding acetyl derivative, $\text{OAc}\cdot\text{C}_3\text{H}_6\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{N}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$, may be prepared by the action of potassium acetate.

This acetyl derivative on hydrolysis breaks up in two ways, yielding as the chief product the hydrochloride of α -amino- δ -hydroxyvaleric acid and a much smaller quantity of pyrrolidine-2-carboxylic acid, together with some glycine hydrochloride.

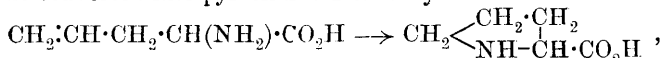
α -Amino- δ -hydroxyvaleric acid, $\text{OH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, crystallises from 80 per cent. alcohol in colourless needles or plates and melts and decomposes at 223—224° (corr.). The acid is readily soluble in water, soluble in aqueous alcohol, slightly soluble in absolute alcohol and acetone, and practically insoluble in ether or light petroleum. On heating at 195—200°, it yields pyrrolidine-2-carboxylic acid, together with other decomposition products. A 35 per cent. yield of this acid is obtained on heating with concentrated hydrochloric acid at 150°.

Glycine is very readily isolated by means of phosphotungstic acid. The same reagent may also be used for the separation of α -amino- δ -hydroxyvaleric acid from pyrrolidine-2-carboxylic acid, since with a 5 per cent. solution of the former it only gives a crystalline precipitate of white needles after 24 hours, whereas with the latter, in 0.5 per cent. solution, it gives at once a characteristic precipitate consisting of short, rhombohedral prisms.

In the esterification of α -amino- δ -hydroxycarboxylic acid by Fischer's method, a portion of the acid is transformed into pyrrolidine-2-

carboxylic acid. The ester is only partially extracted by ether, and when a mixture of the esters of the two acids is distilled, only the pyrrolidinecarboxylic ester distils unchanged, the ester of the other acid undergoing complete decomposition.

Allylglycine was prepared with the object of determining whether it could be converted into pyrrolidine-2-carboxylic acid:



but the conversion was not achieved. Allylglycine forms rhombohedral plates; it has a sweet taste and melts and evolves gas at $250-252^\circ$ (corr.); the substance is fairly soluble in water and practically insoluble in absolute alcohol; it is not precipitated by phosphotungstic acid, although after 24 hours prismatic crystals of some salt are deposited which are readily soluble in water and in alcohol.

P. H.

Oxidation Products of Glycylglycine. LEO POLLAK (*Beitr. chem. Physiol. Path.*, 1905, 7, 16—20).—Glycylglycine (Fischer, Abstr., 1901, i, 675), when oxidised with calcium permanganate at 0° , yields oxalylaminoacetic acid (Kerp and Unger, Abstr., 1897, i, 269), which is hydrolysed by hydrochloric acid into oxalic acid, ammonia, and probably acetic acid.

J. J. S.

Preparation of Taurocholic Acid. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1905, 7, 148—149. Compare Hammarsten, this vol., i, 33).—Pure taurocholic acid may be obtained from ox-bile by the following process. The bile is added to an equal volume of albumin, diluted with 4 to 5 volumes of water and containing hydrochloric acid in order to dissolve globulins. The precipitated albumin taurocholate is removed and washed until the filtrate no longer gives Pettenkofer's test for glycocholic acid. The precipitate is mixed with 2 per cent. hydrochloric acid, well shaken, filtered, and the filtrate saturated with sodium chloride. Any small amounts of albumin are removed and the clear solution mixed with ether and well shaken, when the taurocholic acid begins to crystallise.

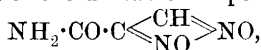
J. J. S.

Constitution of the Fulminuric Acids. CELSO ULPANI (*Gazzetta*, 1905, 35, ii, 7—18).—The compound $(\text{CHON})_n$, obtained by the action of concentrated ammonia solution on the peroxide of ethyl oximinoacetate (compare Ulpiani and Bernardini, Abstr., 1904, i, 971),

is shown to be succinamide dinitrosoperoxide, $\text{NH}_2\cdot\text{CO}\cdot\text{C}\cdot\text{NO}$
 $\text{NH}_2\cdot\text{CO}\cdot\text{C}\cdot\text{NO}$. When boiled with concentrated ammonia solution, it yields (1) the fulminuric acid obtained by Liebig by the action of alkali chlorides on mercuric fulminate, to which the authors ascribe the constitution $\text{NO}_2\text{H}\cdot\text{C}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$; (2) β -isofulminuramide, $\text{NH}_2\cdot\text{C}\cdot\text{N}$
 $\text{NH}_2\cdot\text{CO}\cdot\text{C}\cdot\text{N}$ >O ,

and, as a result of the subsequent hydrolysis of this compound, (3) β -isofulminuric acid, previously obtained by Scholvien (Abstr., 1886, 137) by the action of dilute sulphuric acid on sodium fulminate. The first step in the action of ammonia on succinamide dinitrosoperoxide is

probably the formation of the unstable compound,



which subsequently undergoes further changes, yielding the compounds enumerated above.

β-isoFulminuramide, $\text{C}_3\text{H}_4\text{O}_2\text{N}_4$, separates from water in shining, prismatic crystals melting at 175° , has a neutral reaction, and is practically insoluble in organic solvents. On boiling with alkalis, it gives up ammonia, but it is stable towards mineral acids. When boiled with barium hydroxide solution, it is completely transformed into barium *β*-isofulminurate with evolution of ammonia, and it apparently bears the same relation to *β*-isofulminuric acid as its isomeride described by Ehrenberg (Abstr., 1885, 38) does to isofulminuric acid.

T. H. P.

Imino-CC-dialkylbarbituric Acids. (5:5-Dialkylmalonyl-guanidines.) FIRMA EMANUEL MERCK (D.R.-P. 158890. Compare Abstr., 1904, i, 380; this vol., i, 670—671).—Dialkylmalonyl chlorides react with guanidine in alcoholic solution without the application of heat, forming iminodialkylbarbituric acids (dialkylmalonylguanidines).

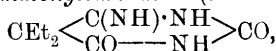
5:5-Diethylmalonylguanidine, $\text{NH}:\text{C} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CEt}_2$, forms colour-

less needles or feathery groups of crystals, and decomposes without melting when heated. The *dipropyl* and *dimethyl* derivatives are similar. Acids readily hydrolyse them to the corresponding dialkylbarbituric acids.

C. H. D.

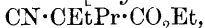
Iminobarbituric and Barbituric Acids. MAX CONRAD (*Annalen*, 1905, 340, 310—325. Compare Michael, Abstr., 1887, 716; Traube, Abstr., 1900, i, 416; 1901, i, 54; 1904, i, 632; Merck, Abstr., 1904, i, 380; this vol., i, 671; Fischer and Dilthey, this vol., i, 35).—In presence of sodium ethoxide, ethyl cyanoacetate and carbamide or thiocarbamide react at the laboratory temperature, and ethyl alkyl- or dialkyl-cyanoacetates and carbamide when warmed, to form iminobarbituric and substituted iminobarbituric acids. These, when heated with mineral acids or formic or acetic acid, are converted into the corresponding barbituric acids. At the laboratory temperature, ethyl cyanodialkylacetates and carbamide react in presence of sodium ethoxide to form cyanodialkylacetylcarbamides. 4-Iminomalonylthiocarbamide (4-amino-6-oxy-2-thiopyrimidine) does not melt at 310° . 4-Iminomalonylguanidine (2:4-diamino-6-oxypyrimidine) melts and decomposes at 286° . 4-Iminomalonyl-3-methylcarbamide (4-amino-2:6-dioxy-3-methylpyrimidine) crystallises in hexagonal leaflets and melts and decomposes at 305° . Malonylmethylcarbamide, $\text{CH}_2 \begin{array}{c} \text{CO} \cdot \text{NMe} \\ \text{CO} - \text{NH} \end{array} \text{CO}$, forms colourless crystals, melts at 133° , and gives the violuric acid reaction with potassium nitrite. 4-Imino-5-propylmalonylcarbamide, $\text{CHPr} \begin{array}{c} \text{C}(\text{NH}) \cdot \text{NH} \\ \text{CO} - \text{NH} \end{array} \text{CO}$, crystallises in glistening, white leaflets, melts and decomposes above 300° , is soluble in hot alcohol or glacial acetic acid, and has both acid and basic properties.

4-Imino-5:5-diethylmalonylcarbamide (*iminoveronal*),



crystallises from water in colourless prisms, melts and decomposes at 295°, and is soluble in aqueous alkali hydroxides or acids; the *hydrochloride*, $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_3\cdot\text{HCl}$, is crystalline.

Ethyl cyanoethylpropylacetate [*α-cyano-α-ethylvalerate*],

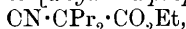


formed by the action of ethyl iodide and sodium ethoxide on ethyl cyanovalerate, boils at 226—229° and has a sp. gr. 0·952 at 15°. 4-

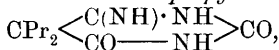
Imino-5-ethyl-5-propylmalonylcarbamide, $\text{CEtPr} \left\langle \begin{array}{c} \text{C(NH)·NH} \\ \text{CO—NH} \end{array} \right\rangle \text{CO},$

melts and decomposes at 301°.

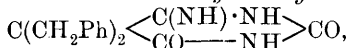
Ethyl dipropylcyanoacetate [*α-cyano-α-propylvalerate*],



prepared by adding propyl iodide to a solution of ethyl cyanoacetate in alcoholic sodium ethoxide, is purified from ethyl cyanoacetate and cyanovalerate by treatment with concentrated aqueous ammonia, with which the latter form soluble amides. It boils at 241—242° and has a sp. gr. 0·937 at 16°/15°. 4-Imino-5:5-dipropylmalonylcarbamide,



crystallises in short prisms and melts and decomposes at 305°. Dipropylbarbituric acid melts at 166° (m. p. 145°; Fischer and Dilthey, *loc. cit.*). 4-Imino-5:5-dibenzylmalonylcarbamide,



melts and decomposes at 295°, and is soluble in dilute hydrochloric acid, from its solution in which it is precipitated on addition of ammonia.

4-Imino-5:5-diethylmalonylguanidine, $\text{CEt}_2 \left\langle \begin{array}{c} \text{C(NH)·NH} \\ \text{CO—NH} \end{array} \right\rangle \text{C:NH},$

formed by warming guanidine hydrochloride with ethyl cyanoethylbutyrate and sodium ethoxide in alcoholic solution, crystallises in long prisms and melts and decomposes at 297° (compare Merck, this vol., i, 670). 4-Imino-5-ethyl-5-propylmalonylguanidine, when boiled with dilute hydrochloric acid, is converted into 5-ethyl-5-propylmalonyl-

guanidine, $\text{CEtPr} \left\langle \begin{array}{c} \text{CO·NH} \\ \text{CO·NH} \end{array} \right\rangle \text{C:NH}$, which crystallises in long, colourless needles, and when boiled with nitric acid or heated with hydrochloric acid at 120—140° yields 5-ethyl-5-propylbarbituric acid.

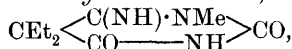
4-Imino-5:5-diethylmalonylthiocarbamide, $\text{CEt}_2 \left\langle \begin{array}{c} \text{C(NH)·NH} \\ \text{CO—NH} \end{array} \right\rangle \text{CS},$

crystallises in yellow prisms, melts and decomposes at 255°, and is converted by boiling dilute hydrochloric acid into 2-thio-5:5-diethylbarbituric acid. This is oxidised by boiling nitric acid of sp. gr. 1·22 to 5:5-diethylbarbituric acid. G. Y.

Iminodialkylmalonylalkyl- and Iminodialkylmalonylphenylcarbamides. MAX CONRAD and A. ZART (*Annalen*, 1905, 340, 326—335. See preceding abstract).—4-Imino-1-methyl-5:5-diethyl-

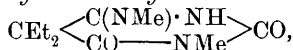
barbituric acid, $\text{CEt}_2 \begin{smallmatrix} \text{C}(\text{NH}) \cdot \text{NH} \\ \text{CO} \text{---} \text{NMe} \end{smallmatrix} \text{CO}$, is formed by boiling 4-imino-5:5-diethylmalonylcarbamide with methyl iodide and sodium ethoxide in alcoholic solution. It crystallises in rhombic leaflets, melts at 258° , is converted into 1-methyl-5:5-diethylbarbituric acid (Fischer and Dilthey, this vol., i, 36) when boiled with dilute mineral acids, and when heated with alcoholic sodium ethoxide in a sealed tube at $150\text{--}160^\circ$ is decomposed into ammonia, carbon dioxide, and *cyanoeethylbutyromethylamide*, $\text{CN} \cdot \text{CEt}_2 \cdot \text{CO} \cdot \text{NHMe}$, which crystallises in long prisms and melts at 102° .

4-Imino-3-methyl-5:5-diethylbarbituric acid,



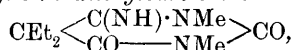
is formed by warming methylcarbamide or acetylmethylcarbamide with ethyl cyanoethylbutyrate and sodium ethoxide in alcoholic solution. It crystallises in needles, melts at 145° , and yields 1-methyl-5:5-diethylbarbituric acid when boiled with dilute mineral acids, and cyanoethylbutyramide, melting at 121° , when heated with sodium ethoxide.

4-Methylimino-1-methyl-5:5-diethylbarbituric acid,

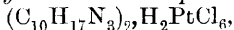


is obtained by boiling 4-imino-1-methyl-5:5-diethylbarbituric acid with methyl iodide and sodium ethoxide in absolute alcoholic solution for 8 hours in a reflux apparatus. It crystallises in hexagonal plates, melts at 212° , and is hydrolysed by boiling dilute hydrochloric acid with formation of methylamine and 1-methyl-5:5-diethylbarbituric acid.

4-Imino-1:3-dimethyl-5:5-diethylbarbituric acid,

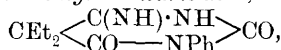


is formed by heating the sodium salt of 4-imino-3-methyl-5:5-diethylbarbituric acid with methyl iodide or methyl sulphate in aqueous alcoholic solution. It crystallises in hexagonal leaflets, melts at 40° , and forms a crystalline *hydriodide* and a *platinichloride*,



which crystallises in short, orange prisms. When heated with hydrochloric acid in a sealed tube at 120° , it yields 1:3-dimethyl-5:5-diethylbarbituric acid, which forms prismatic crystals and melts at 38° .

4-Imino-1-phenyl-5:5-diethylbarbituric acid,



formed by warming phenylcarbamide with ethyl cyanoethylbutyrate and sodium ethoxide in alcoholic solution, crystallises in glistening, white prisms, melts at 222° , and when boiled with 20 per cent. hydrochloric acid is converted into 1-phenyl-5:5-diethylbarbituric acid melting at 175° (m. p. 197° ; Fischer and Dilthey, *loc. cit.*). When heated with sodium ethoxide, 4-imino-1-phenyl-5:5-diethylbarbituric acid is hydrolysed to *cyanoeethylbutyranilide*, $\text{CN} \cdot \text{CEt}_2 \cdot \text{CO} \cdot \text{NHPh}$, which crystallises in long, delicate needles and melts at 122° .

G. Y.

Cyanodialkylacetylcarbamides and the Amides of Substituted Malonic and Cyanoacetic Acids. MAX CONRAD and A. ZART (*Annalen*, 1905, 340, 335—350. Compare preceding abstracts; Mulder, *Abstr.*, 1878, 786; Errera, *Abstr.*, 1896, i, 528).—*α-Cyano-α-ethylbutyrylcarbamide*, $\text{CN}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is formed by the action of ethyl cyanoethylbutyrate and sodium ethoxide on carbamide in alcoholic solution at the ordinary temperature, treatment of the product with glacial acetic acid, and removal of the small amount of iminodiethylbarbituric acid which is formed, by shaking with dilute hydrochloric acid or by boiling with ethyl acetate. It crystallises in white prisms or needles, melts at 118° , and when heated with sodium ethoxide or concentrated sodium hydroxide is converted into 4-imino-5:5-diethylbarbituric acid. *Diethylmalonuramide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is formed along with diethylbarbituric and ureidodiethylmalonic (Fischer and Dilthey, this vol., i, 37) acids, when cyanoethylbutyrylcarbamide is warmed with sulphuric or nitric acid and the product treated with ammonia. It crystallises in colourless prisms and melts at 199° . Ureidodiethylmalonic acid melts with evolution of carbon dioxide and formation of ethylbutyrylcarbamide at 163° . Cyanoethylbutyramide is formed when cyanoethylbutyrylcarbamide or 4-imino-5:5-diethylbarbituric acid is heated with alcoholic sodium hydroxide or sodium ethoxide at 120° . It yields diethylmalonamide (Fischer and Dilthey, *Abstr.*, 1902, i, 269) when warmed at 100° for some hours with sulphuric acid and a little water. This sublimes in long, flat needles and boils with slight decomposition above 360° .

The action of sodium on a mixture of ethyl cyanoethylbutyrate and urethane leads to the formation of *α-cyano-α-ethylbutyrylurethane*, $\text{CN}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, which crystallises in long, thin prisms, melts at 128° , and when warmed with concentrated sulphuric acid decomposes into carbon dioxide and diethylmalonamide.

Cyanovaleramide was obtained on treating crude ethyl cyanopropylvalerate with concentrated ammonia. It melts at 122° (m. p. 118° ; Henry, *Jahresber.*, 1889, 639), and when warmed with sulphuric acid yields propylmalonamide melting at 183° .

α-Cyano-α-propylvalerylcarbamide, $\text{CN}\cdot\text{CPr}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is obtained by treating carbamide with ethyl cyanopropylvalerate in presence of sodium ethoxide. It crystallises in colourless prisms, melts at 101° , and when warmed with sulphuric acid yields dipropylbarbituric acid and *dipropylmalonuramide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CPr}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, which crystallises in slender prisms and melts at 207° .

Cyanopropylvaleramide (Errera, *loc. cit.*) is obtained in similar manner to cyanoethylbutyramide. It melts at 153° and is converted by warming with concentrated sulphuric acid into dipropylmalonamide melting at 214° .

α-Cyano-α-ethylvaleramide, obtained as a by-product in the preparation of 4-imino-5-ethyl-5-propylbarbituric acid, melts at 116° .

The following dibenzyl derivatives were prepared in the same manner as the diethyl compounds: *cyanodibenzylacetylcarbamide*, $\text{CN}\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, melts at 187° ; *cyanodibenzylacetamide* crystallises in prisms and melts at 165° ; *dibenzylmalonamide* crystallises in glistening leaflets and melts at 193° .

The action of sodium ethoxide and ethyl cyanoethylbutyrate on methylcarbamide at the laboratory temperature leads to the formation of *cyanoethylbutyrylmethylcarbamide*, $\text{CN}\cdot\text{CET}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$, which crystallises in thick, rhombic leaflets, melts at 153° , is not soluble in dilute hydrochloric acid, and when heated with sodium ethoxide at $50\text{--}60^\circ$ yields 4-imino-3-methyl-5:5-diethylbarbituric acid, but at $120\text{--}130^\circ$ is converted into cyanodiethylacetamide.

Cyanoethylbutyrylphenylcarbamide, $\text{CN}\cdot\text{CET}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in long, flat prisms, melts at 156° , is insoluble in hydrochloric acid, and when heated with sodium ethoxide in a sealed tube at $130\text{--}150^\circ$ decomposes to ammonia and cyanoethylbutyramide, which is formed also by the action of sodium ethoxide and ethyl cyanoethylbutyrate on aniline and treatment of the product with acetic acid. When warmed with sulphuric acid, this is converted into the anilide and the sulphanilide of malonamic acid. The *anilide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}\cdot\text{NHPh}$, crystallises in white prisms, melts at 132° , and is precipitated from its solution in sulphuric acid immediately on dilution. The *sulphanilide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, separates from the dilute acid solution after one or two days as a white, crystalline mass, has a strong acid reaction, and decomposes carbonates. *Diethylmalonanilic acid*, $\text{NHPh}\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{H}$, obtained by hydrolysis of the amide by means of potassium hydroxide and precipitation of the acid with hydrochloric acid, melts at 105° and decomposes to diethylacetanilide and carbon dioxide at 140° .

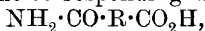
Ethyl diethylmalonamate, $\text{NH}_2\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$, formed by hydrolysis of ethyl cyanoethylbutyrate by means of sulphuric acid, crystallises in needles or large prisms, melts at 79° , and boils without decomposition at 263° .

Hydrolysis of the ester with alcoholic sodium hydroxide leads to the formation of *diethylmalonamic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{H}$, which crystallises in stellate groups of needles and melts and decomposes into carbon dioxide and ethylbutyramide at 146° . It is formed also by warming cyanoethylbutyric acid (Hesse, Abstr., 1897, i, 17) with concentrated sulphuric acid.

Ethyl dipropylmalonamate, $\text{NH}_2\cdot\text{CO}\cdot\text{CPr}_2\cdot\text{CO}_2\text{Et}$, forms crystals, melts at 92° , and forms, as does also the diethylmalonamate, the corresponding barbituric acid when treated with carbamide and sodium ethoxide.

G. Y.

Electrolysis of Imides. ERNESTO PANNAIN (*Gazzetta*, 1905, 35, ii, 94—100).—When an alkaline derivative of an imide is electrolysed under the conditions employed by the author, the imide, $\text{R}\begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix}\text{NH}$, is first transformed into the corresponding amino-acid,



the latter then being hydrolysed to the ammonium salt of the dibasic acid, $\text{CO}_2\text{NH}_4\cdot\text{R}\cdot\text{CO}_2\text{H}$, which is then resolved by the current into ammonia and the acid. Thus, in potassium hydroxide solution, phthalimide yields phthalic acid, succinimide, and succinic acid at the anode.

T. H. P.

Preparation of Mono- and Di-bromoacetonitrile. WILHELM STEINKOPF (*Ber.*, 1905, **38**, 2694—2696).—Bromoacetonitrile (Henry, *Abstr.*, 1886, 1001), boiling at 60—62° under 24 mm. pressure, is formed by the distillation in a vacuum of a mixture of bromoacetamide and phosphoric oxide. The action of chloroacetonitrile on potassium bromide leads to the formation of a product containing only 65.4 instead of 66.67 per cent. of bromine.

Contrary to the statement of van't Hoff (this *Journal*, 1875, 357), the action of bromine on ethyl cyanoacetate leads to the formation of dibromoacetamide, together with a small quantity of a *substance* melting at 86°. Dibromoacetonitrile is formed by distilling in a vacuum a mixture of dibromoacetamide and phosphoric oxide. It is a yellow oil, which has a suffocating odour, attacks the eyes, and boils at 67—69° under 24 mm. pressure. G. Y.

Source of the Excessive Moisture found in certain Combustions. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1905, [iii], **33**, 953—954).—The author describes a number of experiments which show that the source of the water obtained on combustion of certain ferrocyanides and carbonylferrocyanides is the substance burnt, and not errors in the method of combustion. These ferrocyanides and carbonylferrocyanides retain therefore small percentages of water even when dried at 125°. G. Y.

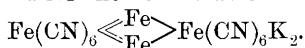
Blue Iron-cyanogen Compounds. II. KARL A. HOFMANN and F. RESENSCHECK (*Annalen*, 1905, **340**, 267—275. Compare Hofmann, Heine, and Höchtlen, this vol., i, 38).—In a neutral solution, a molecular mixture of ferrous sulphate and potassium ferrocyanide forms a white precipitate which is oxidised by the air to a blue soluble in water, but differing from soluble Prussian blue in its behaviour towards oxalic acid. If the white precipitate is formed in presence of 1 per cent. of sulphuric acid, it is more stable towards atmospheric oxygen, and when oxidised forms a stable, soluble blue, which, except for small differences in the content of water, has the same empirical formula, $\text{KFeFeCy}_6\text{H}_2\text{O}$, as soluble Prussian blue and Williamson's violet. This new blue, after being dried over sulphuric acid and finally over phosphoric oxide, is soluble in water or 10 per cent. oxalic acid, forming blue solutions; on addition of ammonia to the aqueous solution, there is formed after some minutes a blue precipitate which becomes green and finally changes into reddish-brown ferric hydroxide; the filtrate from this contains potassium ferrocyanide but no ferrocyanide. On addition of 10 per cent. hydrochloric acid to the aqueous solution, a blue, flocculent precipitate is formed slowly; this is not soluble in water, but behaves like the parent substance towards oxalic acid and ammonia. With ferric chloride, the aqueous solution yields slowly a blue, flocculent precipitate which is soluble in water and is apparently the unchanged soluble blue. In aqueous solution, this stable soluble blue is dissolved in the colloidal state, as shown by the freezing point of the solution being that of water, and by the fact that in an electrical field it travels towards the anode. The optical

properties of the aqueous solution point to the molecule of the new blue as being greater than that of the ordinary soluble blue.

Soluble Prussian blue is soluble in water or oxalic acid even after being dried for some months, but loses its solubility in water when heated at 100° for some hours. It is decomposed to ferric hydroxide and potassium ferrocyanide by 4 per cent. aqueous ammonia in a few seconds, and forms insoluble Prussian blue immediately on addition of ferric chloride. Dilute acids, such as $1\frac{1}{2}$ per cent. sulphuric acid, remove the alkali from soluble Prussian blue, the residue after drying having the composition $2\text{Fe}_2\text{H}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and being insoluble in water but soluble in 10 per cent. oxalic acid.

Williamson's violet does not dissolve in water or oxalic acid, but forms a suspension which is greenish-blue by transmitted, dark purple by reflected, light. It is decomposed by 4 per cent. ammonia after some hours into ferric hydroxide and alkali ferrocyanide, but is not acted on by dilute acids or by aqueous ferric chloride on prolonged digestion.

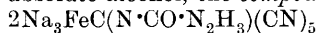
The following constitutional formulæ are suggested: for soluble Prussian blue, $\text{Fe}(\text{OH})_2\text{KH}_2\text{Fe}(\text{CN})_6$; for Williamson's violet, $\text{KFe}(\text{CN})_6 \llcorner \text{Fe} \text{Fe}(\text{CN})_6 \text{K}$, the water always present being probably also constitutional; and for the new soluble stable blue,



A blue, $\text{Fe}_7(\text{CN})_{18} \cdot 10\text{H}_2\text{O}$, having properties similar to those of Williamson's violet, but being less stable towards dilute ammonia, is formed by reducing a mixture of ferric ammonium alum and potassium ferricyanide by means of hydrogen peroxide in presence of free hydrochloric acid. G. Y.

Action of Ketone Reagents on Sodium Carbonylferrocyanide. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1905, [iii], 33, 945—951. Compare Abstr., 1904, i, 147).—Sodium carbonylferrocyanide is not reduced by sodium and absolute alcohol, or by aluminium and acetic acid, or by sodium amalgam and water.

If an aqueous solution of 2 mols. of semicarbazide and 1 mol. of sodium carbonylferrocyanide is evaporated to dryness at 55° and the residue washed with absolute alcohol, the compound



is obtained as a white, crystalline powder, which is easily soluble in water. With cobalt salts, the aqueous solution yields a lilac precipitate, with ferric salts a violet precipitate which rapidly changes into the bluish-violet ferrosferric compound, and with cupric salts a green precipitate, which changes into the colourless cuprous salt. If a molecular solution of sodium carbonylferrocyanide and semicarbazide is evaporated to dryness, the product obtained on washing the residue with alcohol is practically the unchanged sodium salt.

Hydroxylamine has no action on sodium carbonylferrocyanide in aqueous or slightly alkaline solution at 100 — 105° , or in alcoholic sodium ethoxide solution at 170° . But if the sodium salt is boiled with hydroxylamine hydrochloride and an excess of sodium hydroxide

in sufficiently concentrated solution, there is produced a yellow coloration which becomes intensely red and is due probably to formation of the sodium salt of the unstable oxime, $\text{Na}_3\text{FeC}(\text{N}\cdot\text{ONa})(\text{CN})_5$. In moderately alkaline solution, the red colour disappears slowly at the ordinary temperature, quickly on heating, sodium ferrocyanide and a small quantity of ferric oxide being formed. The red colour disappears on acidification with a strong acid, more slowly with a weak acid, and reappears, but less strongly, if the solution is made immediately alkaline. No coloration is formed if the carbonylferrocyanide is replaced by the ferrocyanide or if it is boiled with sodium hydroxide only (compare Simon, *Abstr.*, 1904, ii, 84). On heating sodium carbonylferrocyanide with hydrazine hydrate and sodium hydroxide at $50\text{--}55^\circ$ and washing the residue with alcohol, there is obtained a yellow powder which is easily soluble in water to form a solution which becomes red on heating, and when treated with acetic acid yields sodium carbonylferrocyanide and ferrocyanide and a small quantity of Prussian blue.

No condensation products could be obtained by heating the carbonylferrocyanide with hydrazine, phenylhydrazine, or phenylmethylhydrazine acetates with or without the addition of sodium acetate.

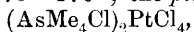
G. Y.

Preparation of Barium Cacodylate. ANGELO ANNONI (*Chem. Centr.*, 1905, ii, 751; from *Boll. Chim. Farm.*, 1905, **44**, 485—488).—In a pure form, the substance can be obtained by pounding together equal parts of crystallised barium hydroxide and cacodylic acid and adding baryta water until the solution reacts feebly alkaline. The decanted and filtered solution is then neutralised with cacodylic acid and evaporated in a vacuum, the residue being afterwards heated for several hours at $115\text{--}120^\circ$ over a mixture of potassium hydroxide, lime, and calcium chloride.

H. M. D.

Tetra-alkylarsonium Bases. EMIL MANNHEIM (*Annalen*, 1905, **341**, 182—233).—The hexa-alkyldiarsonium bases were prepared by Partheil, Amort, and Gronover (*Abstr.*, 1898, i, 351; 1899, i, 474) by the action of alkyl iodides on mercury arsenide. A series of the double salts of the tetra-alkylarsonium bases have been studied and compared with the double salts of the bases prepared according to the directions of the authors just mentioned. It was thus shown that tetra-alkylarsonium bases are formed in this reaction and not hexa-alkyldiarsonium bases, which do not therefore appear to exist.

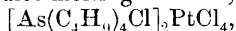
The following double salts of tetramethylarsonium hydroxides have been prepared: the compound $\text{AsMe}_4\text{I}, \text{HgI}_2$ crystallises in yellow needles melting at 184° ; the compound $\text{AsMe}_4\text{Cl}, \text{HgCl}_2$ crystallises in white needles melting at $175\text{--}176^\circ$; the *platinichloride*,



forms yellow crystals decomposing at $250\text{--}260^\circ$; the *aurichloride*, $\text{AsMe}_4\text{Cl}, \text{AuCl}_3$, crystallises in needles melting at 233° . The double salts derived from tetraethylarsonium hydroxide were prepared: the compound $\text{AsEt}_4\text{I}, \text{HgI}_2$ crystallises in yellow needles melting at 112° ; the compound $\text{AsEt}_4\text{Cl}, \text{HgCl}_2$ crystallises in white needles melting at 139° ; the *platinichloride*, $(\text{AsEt}_4\text{Cl})_2\text{PtCl}_4$, forms crystals melting and

decomposing at 224° ; the *aurichloride*, $\text{AsEt}_4\text{Cl}, \text{AuCl}_3$, crystallises in yellow needles melting at 171° . The double salts derived from tetra-*n*-propylarsonium hydroxide are:— $\text{AsPr}_4^{\alpha}\text{I}, \text{HgI}_2$ crystallises in needles melting at 120° ; the compound $\text{AsPr}_4^{\alpha}\text{Cl}, \text{HgCl}_2$ crystallises in white needles melting at 169° ; the *platinichloride*, $(\text{AsPr}_4^{\alpha}\text{Cl})_2\text{PtCl}_4$, forms reddish-yellow crystals melting at 189° ; the *aurichloride*, $\text{AsPr}_4^{\alpha}\text{Cl}, \text{AuCl}_3$, crystallises in needles melting at 127° . Tetraisopropylarsonium iodide, $\text{AsPr}_4^{\beta}\text{I}$, is prepared by heating arsenic with isopropyl iodide for thirty hours at 180° and crystallises in needles with no definite melting point. The following double salts derived from tetraisopropylarsonium hydroxide were prepared: the compound $\text{AsPr}_4^{\beta}\text{I}, \text{HgI}_2$ crystallises in yellow needles melting at 114° ; the compound $\text{AsPr}_4^{\beta}\text{Cl}, \text{HgCl}_2$ crystallises in needles melting at 171° ; the *platinichloride*, $(\text{AsPr}_4^{\beta}\text{Cl})_2\text{PtCl}_4$, forms crystals and decomposes at 211° ; the *aurichloride*, $\text{AsPr}_4^{\beta}\text{Cl}, \text{AuCl}_3$, crystallises in slender needles melting at 186 — 188° .

Tetra-*n*-butylarsonium iodide, $\text{As}(\text{C}_4\text{H}_9)_4\text{I}$, forms crystals without any definite melting point. The double salts derived from tetra-*n*-butylarsonium hydroxide were prepared: the compound $\text{As}(\text{C}_4\text{H}_9)_4\text{I}, \text{HgI}_2$ crystallises in yellow needles melting at 109° ; the *platinichloride*,

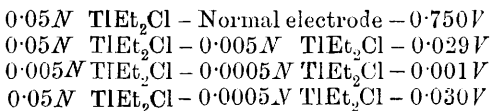


forms yellowish-red crystals decomposing at 220° ; the *aurichloride*, $\text{As}(\text{C}_4\text{H}_9)_4\text{Cl}, \text{AuCl}_3$, crystallises in needles melting at 131° .

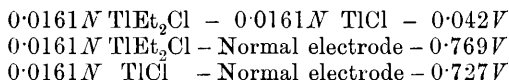
Tetraphenylarsonium chloride was prepared from triphenylarsine and benzyl chloride at 170 — 175° . The following double salts derived from tetraphenylarsonium hydroxide were prepared: the compound $\text{As}(\text{C}_6\text{H}_5)_4\text{I}, \text{HgI}_2$ forms crystals melting at 163° ; the compound $\text{As}(\text{C}_6\text{H}_5)_4\text{Cl}, \text{HgCl}_2$ crystallises in needles melting at 176° ; the *platinichloride*, $[\text{As}(\text{C}_6\text{H}_5)_4\text{Cl}]_2\text{PtCl}_4$, melts at 198° ; the *aurichloride*, $\text{As}(\text{C}_6\text{H}_5)_4\text{Cl}, \text{AuCl}_3$, crystallises in yellow needles melting at about 130° .

The double salts just described are identical with those obtained from mercury arsenide and alkyl iodides. K. J. P. O.

Organo-metallic Compounds. IWAN SHUKOFF (*Ber.*, 1905, 38, 2691—2693).—Tinmethyl bromide (Pfeiffer and Lehnardt, *Abstr.*, 1903, i, 470) has the molecular electrical conductivities $\mu = 700$ — 866 in aqueous solutions with $v = 10$ — 640 . This salt is therefore strongly hydrolytically dissociated in solutions of all strengths. Thallium-diethyl chloride (Meyer and Berthelm, *Abstr.*, 1904, i, 656) is a strong electrolyte, but is hydrolytically dissociated in highly dilute solutions. It has the molecular conductivities $\mu = 84$ — 149 in aqueous solutions with $v = 20$ — 2560 at 25° . When thalliumdiethyl chloride is electrolysed between platinum electrodes, crystalline metallic thallium and a gas consisting to the extent of 15 per cent. of unsaturated hydrocarbons are liberated at the cathode. The concentration of the thallium ions in the thalliumdiethyl chloride solution was determined by measuring the *E.M.F.* of a thallium electrode by the method of compensation:



The influence of dilution is less than that required by Nernst's formula, which appears to be characteristic for thallium salts. Measurements of the *E.M.F.* in thalliumdiethyl chloride solution against a thallium chloride solution saturated at 25° gave the following results :



Applying Nernst's formula to these results, the concentration of the thallium ions in thallium chloride solution is found to be $10^{-2.07}$ whilst that in thalliumdiethyl chloride is $10^{-2.78}$. The thallium-diethyl cation is dissociated therefore to the extent of about 1/300 of its concentration.

G. Y.

Cyclic Compounds. Heptanaphthene (Methylcyclohexane) and its Derivatives. WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1905, **341**, 118—150. Compare Abstr., 1903, i, 19, 157; 1904, i, 383).—Heptanaphthene from naphtha has been compared with that prepared synthetically from the iodide of methylcyclohexanol by reduction with the zinc-copper or the zinc-platinum couple, and purified by treatment with potassium permanganate, nitric and sulphuric acids, sodium, and finally concentrated sulphuric acid. The hydrocarbon boils at 28° under 60 mm. and at 100.2° under 751 mm. pressure; its sp. gr. is 0.7859 at 0°/0°, 0.7697 at 20°/0°, and 0.774 at 15°/15°; it melts at -147.5°. It reacts with bromine in the presence of aluminium bromide forming pentabromotoluene. It is not attacked by nitric and sulphuric acids at 80°, but is oxidised by fuming nitric acid with the formation of succinic acid. Sulphuric acid is without effect, but fuming sulphuric acid oxidises it. Iodine, bromine, and hydriodic acid have little action, whilst potassium permanganate oxidises the hydrocarbon slowly. It was found that the heptanaphthene could not be obtained pure from naphtha.

3-Chloro-1-methylcyclohexane, prepared from pure 1-methylcyclohexanol-3 and fuming hydrochloric acid, boils with decomposition at 63.5—65° under 40 mm. pressure, and has a sp. gr. 0.9664 at 20°/0° and 0.9844 at 0°/0°. The product consists of two stereoisomeric chlorides, of which one is unstable; the chief fraction boils at 69—70° under 40 mm. pressure, and has a sp. gr. 0.98487 at 0°/0°. The stable chloride boils at 160—161° under 756 mm. pressure. The tertiary chloride (1-chloro-1-methylcyclohexane) can be prepared from the corresponding tertiary alcohol (Abstr., 1900, i, 578); it boils at 53—55° under 40 mm. pressure and at 148—151° with decomposition under 752 mm. pressure. The same chloride is obtained by the action of chlorine on heptanaphthene, together with a second chloride which boils at 155.5—157.7° under 740 mm. pressure, and has a sp. gr. 0.960 at 15°/15°. A mixture of two bromides is formed when hydrobromic acid acts either on methylcyclohexanol or on naphthylene; one of these compounds is decomposed on distillation. The stable bromide boils at 181—181.2° under 758 mm. pressure and has a sp. gr. 1.268 at 15°/15°. The corresponding iodide, which also exists in two

isomeric forms, boils at 107° under 40 mm. and at $101\text{--}102^{\circ}$ under 30 mm. pressure, and has a sp. gr. of 1.523 at $15^{\circ}/15^{\circ}$; the same iodide is formed by the action of hydriodic acid on naphthaheptanaphthene chloride. The proof of the constitution of these monohalogen derivatives will be given in a subsequent communication.

K. J. P. O.

Electrolytic Oxidation of Hydrocarbons of the Benzene Series. Part II. Ethylbenzene, Cumene, and Cymene. HERBERT DRAKE LAW and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1905, 1, 251—261).—The chief product obtained by the oxidation of ethylbenzene in sulphuric acid solution containing acetone, using a current density at the anode of 1.3 amperes per sq. cm., was phenylmethylcarbinol; phenylethyl alcohol was also found in small quantity and benzaldehyde made its appearance when the number of ampere hours was more than sufficient to oxidise the whole of the hydrocarbon to alcohol. When oxidised under the same conditions, cymene gave rise to cuminaldehyde and a mixture of mono- and di-hydric alcohols. The carbazone derived from the aldehyde was prepared; it crystallises in pearly plates melting and decomposing at $206\text{--}208^{\circ}$. When cumene boiling at $155\text{--}158^{\circ}$ was oxidised with an anode density of 1.66 amperes per sq. cm., a mixture of cuminaldehyde and hydratropaldehyde, and a mono- and a di-hydric alcohol was obtained.

These experiments confirm the results of earlier experiments carried out with toluene and the xylenes, and indicate that certain groups, for example, the aldehyde group, are relatively stable when acted on electrolytically. The protective action exerted by a negative group is illustrated by the oxidation of cymene, the *isopropyl* group not being attacked to any appreciable extent until the methyl group has been completely converted into the aldehyde group. The conclusion is drawn that the active oxidising agent in the electrolysis of dilute acid and alkaline solutions is the hydroxyl group and not oxygen. Even in acid solution, in consequence of the greater mobility of the hydroxyl ions, there is a tendency for these to concentrate around the anode.

Attempts to obtain phenose, $C_6H_6(OH)_6$, by electrolysis a mixture of benzene, sulphuric acid, and alcohol were unsuccessful. H. M. D.

Replacement of Atoms or Groups of Atoms by Hydrogen in Aromatic Compounds during Reduction. JAN J. BLANKSMA (*Rec. Trav. chim.*, 1905, [ii], 24, 320—326. Compare Loring Jackson, *Abstr.*, 1896, i, 538).—On reduction with tin and hydrochloric acid in alcoholic solution, 1-iodo-2:4-dinitrobenzene, like the corresponding bromo-derivative (compare Zincke and Sintenis, *Abstr.*, 1873, 167), yields *m*-phenylenediamine; 2:4-dinitrobenzenesulphonic acid, like the corresponding benzoic acid (compare Wurster, *Ber.*, 1874, 7, 214), also yields *m*-phenylenediamine on reduction. 2:4:6-Tribromo-*m*-toluidine, when reduced by tin and hydrochloric acid, yields *m*-toluidine, and 2:4:6-tribromo-3:5-dinitrotoluene similarly yields *s*-tolylenediamine (compare Davis, *Trans.*, 1902, 81, 870). 3:5-Dibromo-*l*-dinitrotoluene, melting at 157° (compare Neville and Winther, *Trans.*, 1881, 39, 83),

yields, on reduction with tin and hydrochloric acid, 2 : 4-diaminotoluene whence it follows that the original compound is 3 : 5-dibromo-2 : 4-dinitrotoluene. Nitro-*p*-xylyldinesulphonic acid (compare this vol., i, 426) is reduced by tin and hydrochloric acid to 3 : 5-diamino-*p*-xylene (compare this vol., i, 431). The author therefore draws the conclusion that when an aromatic compound containing a NH_2 group in the ortho- or para-position to the atom or group of atoms (Br , I , CO_2H , SO_3H) is reduced by tin and hydrochloric acid, the latter group is replaced by hydrogen, and this replacement is facilitated by the presence of the group OH , NH_2 , or CH_3 in the meta-position to the NH_2 group.

M. A. W.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. IX. Nitration of *o*-Xylene and its Products.

MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 530—537. Compare Abstr., 1903, i, 269).—*o*-Xylene is slowly attacked in open vessels by nitric acid of sp. gr. 1·075 and more readily by acid of sp. gr. 1·10. Under the same conditions, *p*-xylene is attacked more readily and *m*-xylene with more difficulty. This behaviour leads to a modification of Fittig and Velguth's method for purifying *m*-xylene (*Annalen*, 1868, 148, 10), which is best carried out by boiling and constantly stirring the xylene with nitric acid of sp. gr. 1·075, the concentration being kept constant by the addition of acid; the nitro-compounds are subsequently removed by treating the mass with aqueous potassium hydroxide.

When heated in sealed tubes at 110° with nitric acid of sp. gr. 1·075, *o*-xylene yields *o*-tolylnitromethane, which crystallises in needles melting at 12 — 14° , boils at 145 — 146° under 23 mm. pressure, and has the sp. gr. 1·1572 at $0^\circ/0^\circ$ and 1·1423 at $18^\circ/0^\circ$ and n_D 1·54387 at 18° . *o*-Tolylnitromethane has been prepared by Goldberg (*Abstr.*, 1901, i, 32) and by Wislicenus and Wren (this vol., i, 284), whose divergent results are ascribed by the author to the impurity of their material. When kept, *o*-tolylnitromethane becomes red and deposits a crystalline substance which contains more nitrogen than the original compound and melts at 238 — 242° . The potassium derivative of *o*-tolylnitromethane, $\text{C}_8\text{H}_8\text{K}\cdot\text{NO}_2$, forms shining scales, and its aqueous solution gives the following reactions: with copper sulphate, a dark green precipitate, soluble in ether or benzene, forming a red solution; with silver nitrate, a yellow precipitate, soluble in benzene with a dark red coloration; with mercuric chloride or stannic chloride, a white precipitate. The action of concentrated nitric acid of sp. gr. 1·5 effects substitution in the benzene nucleus of *o*-tolylnitromethane. The latter is reduced by tin and hydrochloric acid, giving the amine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{NH}_2$, melting below 0° and boiling at $205\cdot5$ — 206° under 745 mm. pressure, and having the sp. gr. 0·9921 at $0^\circ/0^\circ$, 0·9776 at $18^\circ/0^\circ$, and 0·9768 at $19^\circ/0^\circ$, and n_D 1·54356 at 19° ; the hydrochloride melts at 219 — 220° , the platinichloride, with decomposition, at 220 — 223° , the hydrobromide at about 209° , the sulphate at 176 — 179° , the nitrate at 130° , the oxalate at 94 — 98° , the picrate at 214 — $215\cdot5^\circ$, and the aurichloride at about 180° .

T. H. P.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons.

X. Nitration in Acetic Acid Solution. MICHAEL I. KONOWALOFF and CH. GUREWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 537—542).—The authors give, in tabular form, the results of the nitration, in presence of acetic acid, of toluene, *o*-, *m*-, and *p*-xylenes, ψ -cumene, ethylbenzene, diethylbenzene, and *tert*-butylbenzene, from which they arrive at the following conclusions: (1) the reactivity of aromatic hydrocarbons with a mixture of nitric and acetic acids obeys the rules already given by Konowaloff (*Abstr.*, 1894, i, 265) for aqueous nitric acid. *tert*-Butylbenzene is most difficult of attack, and then follow *o*- and *p*-xylene, ψ -cumene, ethylbenzene, and diethylbenzene. (2) Like water, acetic acid weakens the action of nitric acid on the aromatic nucleus and, especially on heating, directs the attack to the side-chain. (3) The latter is not only nitrated, but also oxidised, especially when the action of the nitric acid is energetic; acids are then obtained principally. (4) By suitable adjustment of the proportions of nitric and acetic acids, good yields of nitro-compounds substituted in the side-chain can be obtained, and this mixture of acids is sometimes to be preferred to aqueous nitric acid. (5) By using nitric acid, rendered moderately dilute by means of acetic acid, mononitro-compounds substituted in the nucleus can be obtained in cases where concentrated nitric acid acts too energetically. T. H. P.

Diphenylpropanes, especially $\alpha\alpha$ -Diphenylpropane. MICHAEL I. KONOWALOFF and S. DOBROWOLSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 547—551).— $\alpha\alpha$ -Diphenylpropane, $\text{CHPh}_2\cdot\text{CH}_2\text{Me}$, obtained by heating together diphenylethylcarbinol and hydriodic acid of sp. gr. 1.9 in a sealed tube at 140—150°, is a colourless liquid with a blue fluorescence, boils at 278.5—280° under 754 mm. pressure, and has the sp. gr. 0.9938 at 18.5°/0° and n_D 1.56809 at 18.5°.

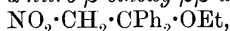
$\alpha\beta$ -Diphenylpropane, prepared by the condensation of allyl chloride and benzene in presence of aluminium chloride, boils at 280—281° under 758 mm. pressure and has sp. gr. 0.9809 at 23.5°/0° and n_D 1.5591 at 23.5°.

$\alpha\gamma$ -Diphenylpropane, prepared by condensing trichlorohydrin and benzene by means of aluminium chloride, boils at 298—299° and has the sp. gr. 1.0071 at 20°/0° and n_D 1.5760 at 20°. T. H. P.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons.

XI. Non-nuclear Nitration of Homologues of Diphenylmethane. MICHAEL I. KONOWALOFF and M. G. JATZEWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 542—547. Compare preceding abstract; *Abstr.*, 1894, i, 265; 1895, i, 633; Anschütz and Romig, *Abstr.*, 1885, 768; 1886, 1033).—On heating pure diphenylethane with nitric acid of sp. gr. 1.075, it yields: (1) an oil; (2) a substance, $\text{C}_{14}\text{H}_{18}\text{O}_3\text{N}$, which separates from acetic acid in colourless, prismatic crystals, or from light petroleum in slender needles melting at 107—108°, and dissolves readily in ether and to a less extent in alcohol; when treated with sodium ethoxide, it gives benzophenone, but with ferric chloride it does not give the reaction for nitro-compounds; on reduction with zinc dust and acetic acid, it yields a base,

$\text{OH}\cdot\text{C}_2\text{H}_2\text{Ph}_2\cdot\text{NH}_2$, which forms white crystals melting at $107-108^\circ$ and gives a *platinichloride*, $(\text{C}_{14}\text{H}_{15}\text{ON})_2\cdot\text{H}_2\text{PtCl}_6\cdot 3\text{H}_2\text{O}$, melting at $146-149^\circ$. On treatment with acetyl chloride, the substance (2) is converted into a yellow, crystalline compound (No. 2 of Anschütz and Romig) which melts at $87-88^\circ$, seems to be saturated, and gives with ferric chloride the reaction for nitro-compounds; on reduction with zinc dust and acetic acid, it yields a syrupy *base*, the hydrochloride of which melts at $170-173^\circ$. The action of sodium ethoxide on the yellow compound melting at $87-88^\circ$ or on the oily product (1) gives the sodium derivative of *α-nitro-β-ethoxy-ββ-diphenylethane*,



which separates from a mixture of ether and light petroleum in large, colourless crystals melting at $91-92^\circ$ and dissolves readily in acetic acid and to a less extent in alcohol or benzene; by its behaviour towards ferric chloride and to Meyer's reaction, it is shown to be a primary nitro-compound; treatment with acetyl chloride gives the original compound melting at $87-88^\circ$, whilst reduction with zinc dust and acetic acid gives an amine, forming a crystalline *platinichloride*, $[\text{OEt}\cdot\text{C}_2\text{H}_2\text{Ph}_2\cdot\text{NH}_2]_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$. The action of sodium amyloxyde on the product melting at $87-88^\circ$ yields a compound which melts at $95-97^\circ$ and is different from *α-nitro-β-ethoxy-ββ-diphenylethane*.

Nitration of diphenylethane with a mixture of nitric and acetic acids yields the same products as are obtained by nitric acid of sp. gr. 1.075.

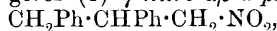
From the above results the authors draw the conclusion that the action on diphenylethane of nitric acid diluted with either water or acetic acid yields nitro-compounds with the nitro-groups in the side-chain.

T. H. P.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. XII. Nitration of Homologues of Diphenylmethane in the Side-chain. MICHAEL I. KONOWALOFF and S. DOBROWOLSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 551-555).—The authors have studied the nitration of *αα*-, *αβ*-, and *αγ*-diphenylpropanes when heated in open vessels with nitric acid of sp. gr. 1.075.

αγ-Diphenylpropane yields primary and secondary nitro-products, the former being probably formed from an isomeric diphenylpropane present as an impurity.

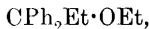
αβ-Diphenylpropane gives (1) *γ-nitro-αβ-diphenylpropane*,



which forms prisms melting at $153-155^\circ$ and dissolves readily in benzene, alcohol, or acetone, and to a less extent in ether; (2) a tertiary nitro-compound, yielding on reduction an amine, the *hydrochloride* of which, $\text{C}_3\text{H}_5\text{Ph}_2\cdot\text{NH}_2\cdot\text{HCl}$, melts at $177-178^\circ$ and the *platinichloride* at 180° .

αα-Diphenylpropane gives products similar to those obtained from the analogous diphenylethane (compare Konowaloff and Jatzewitsch, preceding abstract). The heavy yellow oil obtained gives, with sodium ethoxide, the sodium salt of *β-nitro-α-ethoxy-αα-diphenylpropane* (?),

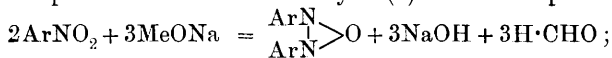
$\text{OEt} \cdot \text{CPh}_2 \cdot \text{CHMe} \cdot \text{NO}_2$, which crystallises from ether in yellow prisms melting at $103\text{--}104^\circ$, is readily soluble in alcohol or benzene, gives Meyer's reaction for secondary nitro-derivatives, and reacts with ferric chloride. There is also formed (1) a tertiary nitro-compound, which yields on reduction an amine, the hydrochloride of which melts at $206\text{--}208^\circ$, and (2) the *ethyl* derivative of *diphenylethylcarbinol*,



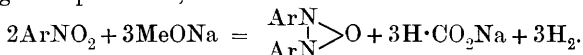
which melts at $160\text{--}161^\circ$.

T. H. P.

Reduction of Nitro-compounds by Alcohols in presence of Alkali. TH. ROTARSKI (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 569—575).—The action of sodium alkyl oxides on aromatic nitro-compounds proceeds in one of two ways: (1) at low temperatures,



(2) at high temperatures,



The author has investigated the reduction of nitrobenzene, *p*-nitro-anisole, and *p*-nitrophenetole by various alcohols in presence of different alkalis. At low temperatures, the action is simply that of hydrogen, so that theoretically there should be formed all reduction products obtainable from either one or two molecules of the nitro-compound. At higher temperatures, the reducing action of alkyl oxides consists only in taking oxygen away from the nitro-compound, so that in this case only compounds poorer in nitrogen can be obtained—azoxy-, azo-, and nitroso-compounds, and not compounds formed by the replacement of oxygen by hydrogen, namely, hydrazo- and amino-compounds, and arylhydroxylamines. In order to increase the yield of azoxy-derivative, which is the chief product of the reaction, the temperature at which the latter is carried out must be raised. The temperature above which one of these reactions and below which the other takes place varies with the nature both of the alcohol and of the nitro-compound and with the amount of alkali present.

The results obtained are summarised by the author as follows: the use of alkali and alcohol has no advantage over that of sodium alkyl oxide for the reduction of nitro-compounds. Aldehydes do not reduce nitro-compounds, even in presence of alkali. The sodium alkyl-oxide may be replaced by barium oxide or hydroxide *plus* an alcohol, but lime, magnesium oxide, or alumina may not be used. If, at the high temperature used for the reduction of nitro-compound to azoxy-compound, the sodium alkyl oxide causes decomposition, barium oxide or hydroxide may be employed with advantage. The alcohol used as a diluent with sodium alkyl oxide may be replaced by other liquids, such as benzene or toluene.

T. H. P.

cycloHexanesulphonic Acid. WALTHER BORSCHÉ and W. LANGE (*Ber.*, 1905, **38**, 2766—2769).—*cyclo*-Hexyl chloride readily forms a Grignard compound with magnesium, and this with dry sulphur dioxide yields magnesium *cyclo*-hexanesulphinate, which is soluble

in water. When oxidised with a cold saturated solution of permanganate, the sulphinate yields dihexamethylene sulphone and *potassium cyclohexanesulphonate*, $C_6H_{11} \cdot SO_2 \cdot OK$. This is readily soluble in water and crystallises from alcohol in glistening plates. The *chloride*, $C_6H_{11} \cdot SO_2Cl$, is a colourless oil distilling at $127-128^\circ$ under 15 mm. pressure, but decomposes when slowly distilled. The *acid* crystallises from alcohol and melts at $90-92^\circ$. The *anilide*, $C_6H_5 \cdot SO_2 \cdot NHPh$, crystallises from dilute alcohol in flat needles and melts at 87° . The *ethyl ester*, obtained by the action of sodium ethoxide on the chloride, is a colourless oil which distils at $150-151^\circ$ under 18 mm. pressure. When reduced, the chloride yields *cyclohexyl hydrosulphide*, $C_6H_{11}SH$.

Dicyclohexanesulphone, $SO_2(C_6H_{11})_2$, is sparingly soluble in hot water and crystallises in colourless needles melting at $132-132.5^\circ$. *Dicyclohexyl* (Abstr., 1902, i, 360) is obtained as a by-product in the preparation of magnesium *cyclohexanesulphinate*. J. J. S.

Action of Pure [Absolute] Nitric Acid on Benzenesulphomethylamide. H. J. BACKER (*Rec. Trav. chim.*, 1905, [ii], 24, 484-491).—When benzenesulphomethylamide is nitrated with fuming nitric acid, the product is benzenesulphomethylnitroamide (compare Van Romburgh, *Rec. Trav. chim.*, 1884, 3, 7), but when pure (absolute) nitric acid is employed, the *m*-nitro-derivative of this compound is produced. *m-Nitrobenzenesulphomethylnitroamide*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NMeNO_2$, can also be formed by the action of pure nitric acid on *m*-nitrobenzenesulphomethylamide (compare Chattaway, *Trans.*, 1905, 87, 159); it forms colourless needles melting at 96° , readily soluble in chloroform, benzene or acetone, warm alcohol, carbon disulphide, or ether, insoluble in light petroleum; on boiling with 10 per cent. potassium hydroxide solution, it yields potassium nitrobenzenesulphonate, from which *m*-nitrobenzenesulphonamide, m. p. $160.5-161^\circ$ (compare Schober and Kiefer, *Abstr.*, 1895, i, 52), is obtained, or the same compound can be prepared by the action of ammonia on the original nitroamide.

M. A. W

Grignard's Reaction. ADOLF VON BAEYER (*Ber.*, 1905, 38, 2759-2765).—Magnesium does not readily react with ethereal solutions of iodo-derivatives of aniline, but the metal may be rendered active by heating in a flask over a free flame and adding gradually about half its weight of iodine, the flask being continually rotated. After treatment in this way, the metal reacts to a slight extent with water, but very vigorously with methyl alcohol, with an ethereal solution of bromobenzene, or with iodo-derivatives of aniline or of dimethylaniline; the reaction is most vigorous with the ortho-compounds, and least with the para. The best method for preparing the magnesium derivatives is to add the active magnesium gradually to the dry ethereal solution of the iodo-derivative. Magnesium *o*-dimethylaminophenyl iodide and methyl dimethylantranilate (Willstätter and Kahn, *Abstr.*, 1904, i, 235) react yielding *tetramethyl-2:2'-diaminobenzophenone*, $C_{17}H_{20}ON_2$, which crystallises from light

petroleum in brilliant yellow prisms melting at 122° . The ethereal solutions of the magnesium iodo-derivatives from the iodo-anilines react readily with benzophenone, yielding aminotriphenylcarbinol derivatives. Magnesium *o*-aminophenyl iodide and methyl benzoate yield benzanilide.

Details for the preparation of the iodo-derivatives of aniline are given. The dimethyl derivatives were prepared by the action of methyl sulphate (Ullmann, Abstr., 1903, i, 394). *o*-Iodoaniline melts at $60-61^{\circ}$, *o*-iododimethylaniline boils at 116° under 11 mm. pressure; *m*-iododimethylaniline melts at $38-39^{\circ}$ and distils at $142-143^{\circ}$ under 12 mm. pressure. *p*-Iodoaniline melts at $67-68^{\circ}$ and the dimethyl derivative at 82° .
J. J. S.

α -Anthramine and α -Anthrol. HANS DIENEL (*Ber.*, 1905, 38, 2862—2867. Compare Liebermann and Simon, Abstr., 1882, 857; Liebermann and Hoermann, *ibid.*, 858; Liebermann and Bollert, *ibid.*, 1105; Liebermann and Hagen, *ibid.*, 1212; Iljinsky, Abstr., 1904, i, 176; Schmidt, *ibid.*, 256).—Ammonio-zinc anthracene-1-sulphonate, $(C_{14}H_9SO_3)_2Zn \cdot 2NH_3 \cdot H_2O$, crystallises in needles from the ammoniacal mother liquors from the reduction of anthraquinone-1-sulphonate with zinc dust and ammonia; when treated with water, it decomposes with formation of zinc dust.

1-Anthrol, formed by fusing potassium anthracene-1-sulphonate with potassium hydroxide at $250-260^{\circ}$, crystallises in brown leaflets or needles, sinters at 146° , and melts and decomposes at $150-153^{\circ}$. It dissolves in the ordinary solvents more easily than does 2-anthrol, to form solutions with blue fluorescence; the solution in aqueous ammonia is green, in dilute alkali hydroxides or baryta yellow with green fluorescence; with traces of nitric acid, the solution in glacial acetic acid forms a dark red coloration, with ferric chloride a green precipitate. The *acetyl* derivative crystallises in colourless needles, becomes brown at about 80° , melts and decomposes at $128-130^{\circ}$, and is oxidised by chromic acid in hot acetic acid solution to erythro-1-acetoxyanthraquinone, $C_{14}H_{17}O_2 \cdot OAc$, which crystallises in glistening, golden needles melting at $175-178^{\circ}$. The *ethyl ether*, $C_{16}H_{14}O$, formed by boiling 1-anthrol with alcoholic hydrogen chloride in a reflux apparatus, crystallises in colourless needles, melts at 69° , and dissolves in alcohol to form a solution with blue fluorescence; the *methyl ether* crystallises in colourless leaflets and melts at 70° . These ethers are formed more slowly and in poorer yields and melt at lower temperatures than the corresponding 2-compounds.

1-Anthramine, $C_{14}H_9 \cdot NH_2$, formed by heating 1-anthrol with acetamide in a sealed tube at 260° , crystallises in glistening, yellow leaflets, melts at about 130° , is more soluble than the 2-amine, gives the same colour reactions with bromine and concentrated nitric acid, but a greyish-green coloration with arsenic acid, and has only weak basic properties. The *hydrochloride*, $C_{14}H_{11}N \cdot HCl$, and the sulphate are white, crystalline substances. The *acetyl* derivative, $C_{14}H_{11}N \cdot Ac$, crystallises in green needles, melts at 198° , and is oxidised to α -acetylaminoanthraquinone by chromic acid in glacial acetic acid solution.

Dihydro-1-anthramine, $C_6H_4 \begin{smallmatrix} <CH_2 \\ <CH_2 \end{smallmatrix} C_6H_3 \cdot NH_2$, formed by reduction of 1-anthramine with sodium amalgam in boiling alcoholic solution, crystallises in slender, glistening, colourless needles, has an odour of dihydroanthracene, and sinters at $60-70^\circ$, but has no sharp melting point. The *hydrochloride*, $C_{14}H_{13}N \cdot HCl$, forms glistening leaflets.

Di-1-anthramine, $NH(C_{14}H_9)_2$, is formed when 1-anthramine is boiled with glacial acetic acid in a reflux apparatus. It crystallises in glistening leaflets, melts at 204° , is insoluble in concentrated hydrochloric acid, and is less volatile and less soluble than 1-anthramine.

G. Y.

Bromine Additive Compounds of Dimethylaniline. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1905, **34**, 261—290).—The following nomenclature is suggested for the compounds described in this paper. Additive compounds containing the bromine attached to a carbon atom of the benzene nucleus are termed benzbromides; if the bromine is united to the nitrogen, the compounds are amine dibromides (or hydrobromides); and when the additive bromine is attached to a bromine atom, the compounds are termed perbromides.

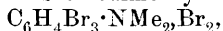
Fries (*Abstr.*, 1904, i, 571) has already obtained certain bromine additive compounds of dimethylaniline by adding bromine to a solution of dimethylaniline or its hydrobromide in glacial acetic acid. The compounds now described were prepared by the addition of bromine to dimethylaniline dissolved in chloroform.

3 : 4-Dibromodimethylaminodihydrobenzene (benz-3 : 4-dibromide of dimethylaniline), $C_6H_5Br_2 \cdot NMe_2$, crystallises in long, slightly yellow plates or slender needles, melts at about 82° , is soluble in alcohol, chloroform, or acetone, and on exposure to the air is slowly converted into *p*-bromodimethylaniline; it dissolves in dilute acids, does not liberate iodine from potassium iodide, and is turned reddish-brown by quinone. When this substance is treated with excess of ethyl bromide, the additive compound (benz-3 : 4-dibromide of dimethylethylphenylammonium bromide), $C_6H_5Br_2 \cdot NMe_2EtBr$, is produced, which crystallises in flat, white prisms, and by the action of water is converted into a red oil.

3 : 4-Dibromodimethylaminodihydrobenzene dibromide (benz-3 : 4-dibromide of dimethylaniline dibromide), $C_6H_5Br_2 \cdot NMe_2Br_2$, crystallises in long, yellowish-red needles, melts at $65-70^\circ$, is soluble in alcohol, chloroform, acetone, or ethyl acetate, is insoluble in dilute acids, and is converted by potassium hydroxide into dibromodimethylaniline; it dissolves in ethyl bromide and crystallises unchanged from the solution, and gives a blue coloration with potassium iodide and starch paste. When this substance is treated with acetone, it is converted into 3 : 4-dibromodimethylaminodihydrobenzene, whilst by the action of alcohol the *hydrobromide* of dibromodimethylaniline is produced, which melts at 110° . When 3 : 4-dibromodimethylaminodihydrobenzene dibromide is moistened with chloroform, it gradually changes into a red substance, $C_{10}H_{24}N_2Br_7$, which contains one atom of bromine capable of replacing iodine in potassium iodide and melts at 105° ;

it is not identical with the compound $(C_6H_3Br_2 \cdot NMe_2, HBr)_2Br$, described by Fries (*loc. cit.*). By the action of hot chloroform on the dibromide, a viscous substance is produced which does not react with potassium iodide, is converted by sodium thiosulphate into dibromodimethylaniline, and is probably the compound $C_6H_4Br_3 \cdot NMe_2, HBr$; if left for several days, it changes into a red compound similar to that already described, and becomes capable of liberating iodine from potassium iodide.

Tetrabromodimethylaminotetrahydrobenzene dibromide (benztetrabromide of dimethylaniline dibromide), $C_6H_5Br_4 \cdot NMe_2, Br_2$, crystallises in small, red needles and is very unstable; it readily loses hydrogen bromide, becoming converted into *tribromodimethylaminodihydrobenzene dibromide* (benzdibromide of bromodimethylaniline dibromide),



which forms long, red prisms, melts at 78° , and is converted by potassium hydroxide into dibromodimethylaniline. By the action of acetone on the compound last described, an oily *substance* is formed which does not react with potassium iodide and is probably the benzdibromide of bromodimethylaniline, $C_6H_4Br_3 \cdot NMe_2$. When the compound containing five bromine atoms is treated with alcohol, it is converted into a substance which is probably identical with the *o-p*-dibromodimethylaniline hydrobromide perbromide described by Fries (*loc. cit.*). The compound reacts with aniline with formation of aniline hydrobromide, dibromodimethylaniline, and small quantities of a *substance* which forms red crystals, whilst when treated with a mixture of potassium iodide and sodium thiosulphate it is converted into *p*-bromodimethylaniline. If a solution of the substance in chloroform is treated with solid potassium iodide, the *compound*



is formed, which crystallises in reddish-yellow prisms and melts at 137° . By the action of sodium acetate on the benzdibromide of dimethyl-*p*-bromoaniline dibromide, dibromodimethylaniline is produced.

When bromine is added to a chloroform solution of *p*-bromodimethylaniline, the compound $C_6H_3Br_2 \cdot NMe_2, HBr, Br_2$ (Fries, *loc. cit.*) is obtained. By the action of bromine on dibromodimethylaniline, the *perbromide*, $C_6H_3Br_2 \cdot NMe_2, HBr_4$, is formed, which crystallises in yellowish-red, flat prisms, melts at 98° , is converted by acetone into the hydrobromide of dibromodimethylaniline, by potassium hydroxide into dibromodimethylaniline, by cold alcohol into the perbromide,



(Fries, *loc. cit.*), and by hot alcohol or chloroform into *tribromodimethylaniline hydrobromide*, which darkens at 200° and melts at 202° .

p-Bromodimethylaniline di-iodide, $C_6H_4Br \cdot NMe_2, I_2$, obtained by the action of iodine on a chloroform solution of *p*-bromodimethylaniline, crystallises in flat, black prisms, melts at 115° , and is slightly soluble in alcohol, acetone, or ethyl acetate.

E. G.

ω -Sulphomethyl Derivatives of Aromatic Amines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 158718. Compare this vol., i, 340).—Diphenylamine reacts with formaldehyde and sodium hydro-

gen sulphite: $\text{CH}_2(\text{NPh}_2)_2 + \text{HSO}_3\text{Na} = \text{NPh}_2 \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na} + \text{NHPH}_2$. The *sodium* salt thus obtained separates in glistening, colourless needles. Potassium chloride precipitates the sparingly soluble *potassium* salt. The *ω*-sulphonic acid is stable, and reacts with metallic cyanides to form the viscous *nitrile*. C. H. D.

Preparation of *α*-Phenyl- and *p*-Tolyl-naphthylamine-6- and -7-sulphonic Acids. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 159353).—In addition to *α*-naphthylamine-4 : 8-disulphonic acid (this vol., i, 717), *α*-naphthylamine-4 : 6- and -4 : 7-disulphonic acids also lose the 4-sulphonic group when heated with aniline or *p*-toluidine at 180°, arylation of the amino-group taking place at the same time, yielding *α*-phenyl- or *α*-*p*-tolyl-naphthylamine-6- or -7-sulphonic acid. C. H. D.

Action of Formaldehyde on Thiocarbanilide. ERICH OPFERMANN (*Chem. Zeit.*, 1905, 29, 1075—1076).—A mixture of finely powdered thiocarbanilide with formaldehyde was treated with dry hydrogen chloride until all the thiocarbanilide had dissolved; the substance obtained, on treatment with excess of ice-cold water, gave a white, flocculent precipitate which could not be purified; the acid filtrate from the latter, when made alkaline with sodium hydroxide, deposited a substance which crystallised from alcohol in groups of needles melting at 78°, and was readily soluble in cold benzene, ether, acetone, or chloroform; it was decomposed by solution in hot 30 per cent. sulphuric acid. Molecular weight determinations gave the values 239 and 246, and these, combined with the analytical results, lead to the formula $\text{NPh} \cdot \text{C} \begin{smallmatrix} \text{S} - \text{CH}_2 \\ \text{NPh} \cdot \text{CH}_2 \end{smallmatrix} \text{O}$. The corresponding derivatives obtained from *π*-chloro- and *π*-bromo-thiocarbanilide melt at 84° and 80° respectively. The former crystallises from alcohol in small, white plates, and the latter in white, transparent plates. P. H.

Preparation of *β*-Arylhydroxylamines by the Electrochemical Reduction of Aromatic Nitro-compounds. KURT BRAND (*Ber.*, 1905, 38, 3076—3078).—A fine suspension of nitrobenzene in an aqueous solution of acetic acid and sodium acetate is placed in a porous pot, which serves as the cathode vessel and is kept automatically stirred. The pot is surrounded by a lead pipe which serves as anode and through which cold water is passed, so that the temperature is kept at 20—25°. The whole is placed in a glass vessel containing dilute sulphuric acid. The cathode is a nickel wire gauze of 3—4 sq. cm. surface, and a voltage of 6—8 with a current of 6—10 amperes yields the best results. From 50 grams of nitrobenzene 32 grams of phenylhydroxylamine have been obtained, together with a trace of azoxybenzene and a little aniline.

p-Chlorophenylhydroxylamine has been prepared in a similar manner using an alcoholic solution of the nitro-compound mixed with an aqueous solution of acetic acid and sodium acetate. J. J. S.

Action of Phenylcarbimide on Sulphonic Acids. C. VALLEE (*Bull. Soc. chim.*, 1905, [iii], 33, 966—969).—Haller has shown that organic acids react with phenylcarbimide to form diphenylcarbamide and the anilide of the acid. It is now found that sulphonic acids and phenylcarbimide form principally the aniline sulphonates, with little diphenylcarbamide and no anilide.

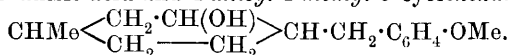
A comparison of the products obtained by the interaction of phenylcarbamide and acetic and chloro-, dichloro-, and trichloroacetic acids in *N*-aqueous solution with those obtained with benzenesulphonic acid in *N*/2·4 solution shows that the amount of aniline salt formed increases, whilst that of the diphenylcarbamide decreases, with increasing affinity of the acid.

	Affinity, HCl=100.	Of 100 grams of phenylcarbimide, there were recovered from the product as		
		Aniline salt.	Anilide.	Diphenyl- carbamide.
Acetic acid, <i>N</i>	0·4	5·58	0·0	94·41
Chloroacetic acid	4·8	20·00	4·66	75·33
Dichloroacetic acid	27·0	30·16	14·11	58·41
Trichloroacetic acid	75·0	51·83	traces	48·16
Benzenesulphonic acid, <i>N</i> /2·4...	104·0	91·66	0·0	8·33

These results are due to the varying ionisation of the acids, as is shown by the formation of the anilide only without any aniline salt by the action of phenylcarbimide on trichloroacetic acid in *N*-toluene solution. G. Y.

Action of Aromatic Aldehydes on Sodium 1-Methyl-3-cyclohexanoxide. ALBIN HALLER and FRANÇOIS MARCH (*Bull. Soc. chim.*, 1905, [iii], 33, 969—974. Compare this vol., i, 276; Haller, *Abstr.*, 1900, i, 301; Martini, *Abstr.*, 1904, i, 903).—The action of 1 mol. of sodium 1-methyl-3-cyclohexanoxide in toluene solution on more than 2 mols. of benzaldehyde, cooled by ice, leads to the formation of 4-hydroxybenzyl-1-methyl-3-cyclohexanol (Tetry, *Abstr.*, 1902, i, 469), benzyl alcohol, dibenzylidene-1-methyl-3-cyclohexanol, melting at 127°, and 1-methyl-3-cyclohexanyl benzoate, $C_{14}H_{18}O_2$, which melts at 66—67° and is easily soluble in ether, alcohol, or light petroleum. This may be formed also by the action of benzoyl chloride on sodium methylcyclohexanoxide or on methylcyclohexanol in presence of piperidine. The action of 1 mol. of sodium 1-methyl-3-cyclohexanoxide on 1 mol. of benzaldehyde in toluene solution, the mixture being heated to complete the reaction, leads to the formation of 4-benzyl-1-methyl-3-cyclohexanol and a small amount of sodium benzoate.

Similarly, the action of 1 mol. of sodium 1-methyl-3-cyclohexanoxide on 2 mols. of anisaldehyde in the cold leads to the formation of anisyl alcohol and 4-anisylidene-1-methyl-3-cyclohexanone, but on 1 mol. of anisaldehyde, and with heating to complete the reaction, to the formation of anisic acid and 4-anisyl-1-methyl-3-cyclohexanol,



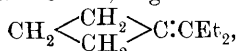
This is obtained as a white powder, melts at 93—94°, and has $[\alpha]_D + 6^\circ 30'$ in alcoholic solution.

4-*Anisyl-1-methyl-3-cyclohexanone*, $C_{15}H_{20}O_2$, formed by reduction of the anisylidene compound with sodium amalgam in presence of alcohol, melts at $52-53^\circ$, and on reduction with sodium and alcohol yields anisylmethylcyclohexanol. G. Y.

cycloButyldimethylcarbinol and its Transformations. NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 509—517).—*cycloButyldimethylcarbinol*, $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH \cdot CMe_2 \cdot OH$, prepared by Masson's method (*Abstr.*, 1901, i, 249) by the action of magnesium methiodide on ethyl *cyclobutanecarboxylate*, is a mobile liquid with an odour resembling that of camphor, and boils at 147° , has the sp. gr. 0.8952 at $20^\circ/0^\circ$, and n_D 1.4457 at 20° . The action of hydrogen bromide on the alcohol yields two bromides: (1) one, which was not isolated, giving, under the action of alcoholic potassium hydroxide, a *hydrocarbon*, $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>C \cdot CMe_2$, boiling at $100-102^\circ$ under 753 mm. pressure, and having the sp. gr. 0.7852 at $20^\circ/0^\circ$ and n_D 1.4371 at 20° ; (2) the *bromide*, $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH \cdot CMe_2 Br$, which is a colourless liquid turning yellow, and later dark green, when kept, and which boils at 167° under 755 mm. pressure, has the sp. gr. 1.2562 at $20^\circ/0^\circ$ and n_D 1.4796 at 20° ; when reduced by means of the copper-zinc couple in alcohol, it yields a *hydrocarbon* which is probably 1:1-dimethylcyclopentane, $CMe_2<\begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix}>$, and boils at $88.3-88.5^\circ$ under 756 mm. pressure, and has sp. gr. 0.7553 at $20^\circ/0^\circ$ and n_D 1.4132 at 20° . On heating with hydriodic acid at 225° , *cyclobutyldimethylcarbinol* yields 1:3-dimethylcyclopentane. T. H. P.

cycloButyldiethylcarbinol and its Compounds. NIC. M. KIJNER and W. AMOSOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 517—520).—*cycloButyldiethylcarbinol*, $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH \cdot CEt_2 \cdot OH$, prepared by Masson's method (*Abstr.*, 1901, i, 249) by the action of magnesium ethiodide on ethyl tetramethylenecarboxylate, is a viscous liquid boiling at $188-189^\circ$ under 759 mm. pressure, and having the sp. gr. 0.9176 at $0^\circ/4^\circ$ and 0.9010 at $20^\circ/4^\circ$ and n_D 1.4554 at 20° .

When distilled with oxalic acid, it gives the *hydrocarbon*,



which has sp. gr. 0.8092 at $20^\circ/0^\circ$ and n_D 1.4510 at 20° . When shaken with concentrated sulphuric acid, this compound passes into *cyclobutyldiethylmethane*, $CH_2<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>CH \cdot CHEt_2$, which boils at $151-152^\circ$ under 775 mm. pressure and has sp. gr. 0.7946 at $19^\circ/0^\circ$ and n_D 1.4334 at 20° .

Reduction of *cyclobutyldiethylcarbinol* by means of hydriodic acid gives a *hydrocarbon*, C_9H_{18} , which boils at $148-149^\circ$ under 767 mm. pressure, and has sp. gr. 0.7851 at $20^\circ/0^\circ$ and n_D 1.4298 at 20° .

T. H. P.

Triphenylcarbinols. HUGO KAUFFMANN and AD. GROMBACH (*Ber.*, 1905, **38**, 2702—2706. Compare this vol., i, 280; Gomberg, *Abstr.*, 1902, i, 534).—When boiled with alcoholic zinc chloride (compare Ullmann and Mourawiew-Winogradoff, this vol., i, 642), diphenyl-2:5-dimethoxyphenylcarbinol yields *diphenyl-2:5-dimethoxyphenylmethane*, $C_{21}H_{20}O_2$, which crystallises in white needles, melts at 104° , and gives a yellow coloration with concentrated sulphuric acid. With this acid, the carbinol gives an emerald-green coloration. If the carbinol is boiled for more than a few minutes with alcoholic zinc chloride, in the place of the methane there are obtained a liquid *product* which has an odour resembling that of safrole and is volatile in a current of steam, and a solid *substance*, which melts at 192° and is only slightly soluble in alcohol.

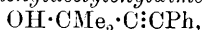
Diphenyl-2:5-dimethoxyphenylmethyl chloride, $C_6H_5(OMe)_2 \cdot CPh_2Cl$, is formed when a current of hydrogen chloride is passed through a benzene solution of the carbinol containing anhydrous sodium sulphate, and the green solution so obtained is distilled finally in a vacuum. It crystallises from light petroleum in white needles, melts at 98° , reacts easily with traces of moisture, and when boiled with alcohol is reduced to diphenyl-2:5-dimethoxyphenylmethane. This is formed directly by the action of hydrogen chloride on the carbinol covered with warm alcohol; if the green alcoholic solution so formed is concentrated too far, a *second* modification of diphenyl-2:5-dimethoxyphenylmethane separates on cooling as an oil. This solidifies to crystals which melt and change into the first modification at 84° . The more fusible form is produced also from the less fusible by crystallisation from a super-cooled, highly concentrated alcoholic solution.

In the formation of the methane from the carbinol or its chloride, in presence of alcohol, the latter is oxidised to acetaldehyde.

Diphenyl-2:5-dimethoxyphenylmethane, melting at 104° , is obtained also when the carbinol is reduced by zinc dust in boiling glacial acetic acid solution. When heated with alcoholic zinc dust, triphenylcarbinol yields triphenylmethane. G. Y.

Action of Potassium Hydroxide on Mixtures of Ketones with Phenylacetylene. ALEXEI E. FAWORSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 643—645).—The action of anhydrous potassium hydroxide on a mixture of a ketone with phenylacetylene yields an unsaturated alcohol, the reaction taking place in two stages: the potassium hydroxide is first added to the carbonyl group of the ketone, $>C:O + KOH = >C(OH) \cdot OK$, the latter then gradually reacting with the phenylacetylene according to the equation $>C(OH) \cdot OK + CH:CPh = >C(OH) \cdot C:CPh + KOH$. The reaction is hence similar to that occurring between potassium hydroxide, a ketone, and chloroform, which also takes place in two stages, the group $>C(OH) \cdot OK$, formed in the first, reacting with the chloroform, thus: $>C(OH) \cdot OK + CHCl_3 = >C(OH) \cdot CCl_3 + KOH$. In this case, however, the yields obtained are not so good as in the above synthesis of unsaturated alcohols, in which water can be almost completely excluded. T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Acetone: Synthesis of Phenylacetylenyldimethylcarbinol. M. SKOSSAREWSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 645—647).—*Phenylacetylenyldimethylcarbinol*,



prepared by gradually adding finely-powdered potassium hydroxide to a mixture of phenylacetylene (1 mol.) and acetone (1 mol.) diluted with an equal volume of ether and cooled to 0° , separates from ether in colourless crystals melting at 53° . It forms an *acetyl* derivative, $\text{C}_{13}\text{H}_{14}\text{O}_2$, boiling at $130\text{--}135^\circ$ under 10 mm. pressure. When heated with 5 per cent. sulphuric acid solution, the alcohol yields a *hydrocarbon*, $\text{CH}_3 \cdot \text{CMe} \cdot \text{C} : \text{CPh}$, boiling at 88° under 7 mm. pressure. When boiled with aqueous potassium hydroxide, phenylacetylenyldimethylcarbinol yields acetone and phenylacetylene. T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene with Methyl Ethyl Ketone: Synthesis of Phenylacetylenylmethylethylcarbinol. IWAN BORK (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 647—650. Compare preceding two abstracts).—*Phenylacetylenylmethylethylcarbinol*, $\text{OH} \cdot \text{CMeEt} \cdot \text{C} : \text{CPh}$, prepared by the interaction of potassium hydroxide, methyl ethyl ketone, and phenylacetylene, is a syrupy liquid with a pleasant odour recalling that of rose-oil; it boils at $129\text{--}130^\circ$ under 9 mm. pressure, and has the sp. gr. 1.0039 at $0^\circ/0^\circ$ and 0.9906 at $20^\circ/20^\circ$. On boiling with 10 per cent. potassium hydroxide solution, it is resolved into methyl ethyl ketone and phenylacetylene. When boiled with 5 per cent. sulphuric acid solution, it yields the *hydrocarbon*, $\text{CHMe} \cdot \text{CMe} \cdot \text{C} : \text{CPh}$, as a liquid which has a smell resembling that of honey, boils at $102\text{--}103^\circ$ under 9 mm. pressure, and has the sp. gr. 0.9462 at $0^\circ/0^\circ$ and 0.9305 at $20^\circ/20^\circ$; on treatment with concentrated sulphuric acid at the ordinary temperature and then with water, the hydrocarbon undergoes hydration to phenylacetylenylmethylethylcarbinol, the water being added at the double and not at the treble linking.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Methyl *iso*Propyl Ketone: Synthesis of Phenylacetylenylmethylisopropylcarbinol. IWAN BORK (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 650—652. Compare preceding abstracts).—*Phenylacetylenylmethylisopropylcarbinol*, $\text{CHMe}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{C} : \text{CPh}$, prepared by the interaction of phenylacetylene and methyl *iso*propyl ketone in presence of potassium hydroxide, melts at 41° and boils at $136\text{--}137^\circ$ under 12 mm. pressure. On boiling with 10 per cent. potassium hydroxide solution, it is resolved into phenylacetylene and methyl *iso*propyl ketone. When boiled with 5 per cent. sulphuric acid solution, it yields a *hydrocarbon*, $\text{CMe}_2 \cdot \text{CMe} \cdot \text{C} : \text{CPh}$, which is a mobile liquid boiling at $120\text{--}122^\circ$ under 12 mm. pressure, and having the sp. gr. 0.9409 at $0^\circ/0^\circ$ and 0.9254 at $20^\circ/20^\circ$.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Pinacolin: Synthesis of Phenylacetylenylmethyltert.-butylcarbinol. N. NEWEROWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 652—654. Compare preceding abstracts).—*Phenylacetylenylmethyltert.-butylcarbinol*, $\text{CMe}_3 \cdot \text{CMe}(\text{OH}) \cdot \text{C} \cdot \text{CPh}$, obtained by the action of potassium hydroxide on a mixture of phenylacetylene and pinacolin, is an oily liquid boiling at $135\text{--}136^\circ$ under 10 mm. pressure and having the sp. gr. 0.9855 at $0^\circ/0^\circ$ and 0.9694 at $20^\circ/20^\circ$. When boiled with 10 per cent. potassium hydroxide solution, the alcohol is decomposed into phenylacetylene and pinacolin.

Dehydration of the alcohol by means of 5 per cent. sulphuric acid solution yields a *hydrocarbon*, $\text{CH}_3 \cdot \text{C}(\text{CMe}_3) \cdot \text{C} \cdot \text{CPh}$, which is a mobile liquid boiling at $115\text{--}116^\circ$ under 10 mm. pressure, and gradually changing into a solid polymeride when kept in a sealed tube.

T. H. P.

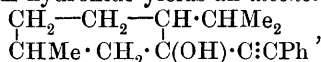
Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Methylcyclohexanone. EW. BERTROND (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 655—656).—The interaction of phenylacetylene and methylcyclohexanone in presence of potassium hydroxide yields an *alcohol*, $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \right\rangle \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CPh}$, which crystallises from ether in thin, silky needles melting at 99° and dissolves slightly in alcohol. When heated with fused potassium hydrogen sulphate in a sealed tube, it yields resinous products and a *hydrocarbon*, $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CHMe} \cdot \text{CH} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \right\rangle \text{C} \cdot \text{C} \cdot \text{CPh}$ or $\text{CH}_2 \left\langle \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH} \end{smallmatrix} \right\rangle \text{C} \cdot \text{C} \cdot \text{CPh}$, which boils at $167\text{--}168^\circ$ under 10 mm. pressure.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Acetophenone. EW. BERTROND (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 657).—The tertiary alcohol, $\text{OH} \cdot \text{CMePh} \cdot \text{C} \cdot \text{CPh}$, obtained by the interaction of phenylacetylene and acetophenone in presence of potassium hydroxide, is identical with the compound obtained by Nef (Abstr., 1900, i, 20) as the result of the action of the sodium derivative of phenylacetylene on acetophenone.

T. H. P.

Action of Potassium Hydroxide on a Mixture of Phenylacetylene and Menthone. E. ROMANOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 657—659).—The action of phenylacetylene on menthone in presence of potassium hydroxide yields an *alcohol*,



which is a viscous, pale yellow liquid with a smell resembling that of menthone and a bitter taste; it boils at $196\text{--}198^\circ$ under 14 mm. pressure, and has the sp. gr. 1.00449 at $0^\circ/0^\circ$ and 0.99056 at $20^\circ/20^\circ$. On boiling with 10 per cent. potassium hydroxide solution, the alcohol is resolved into menthone and phenylacetylene, but it could not be dehydrated into the corresponding unsaturated hydrocarbon.

T. H. P.

Reversible Isomeric Process taking place between γ -Phenylpropylene and s -Phenylmethylethylene [α -Phenylpropylene] on heating with Anhydrous Alkali Hydroxide. M. AGEWA (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 662—668).—Treatment of γ -phenylpropyl alcohol with phosphorus and iodine yields the corresponding *iodide*, which is a viscous, pale rose-coloured liquid boiling at 127—129° under 9—10 mm. pressure, and having the sp. gr. 1.5781 at 0°/0° and 1.5613 at 20°/0°. When heated with anhydrous potassium hydroxide in a copper vessel, the iodide yields: (1) the *ether*, $(\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$, which is a yellow liquid boiling at 220—222° under 19 mm. pressure, and having the sp. gr. 1.00797 at 0°/0° and 0.99488 at 17°/0°; the ether has the normal molecular weight in freezing benzene, and when heated with hydriodic acid gives the original iodide; (2) γ -phenylpropylene, $\text{CH}_2\text{Ph}\cdot\text{CH}\cdot\text{CH}_2$, which boils at 157—160° and has the sp. gr. 0.90706 at 0°/0° and 0.8929 at 20.5°/0°; with bromine it gives $\beta\gamma$ -dibromo- α -phenylpropane, $\text{CH}_2\text{Ph}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, which boils at 136—137° under 8 mm. pressure and has the sp. gr. 1.6902 at 0°/0° and 1.6613 at 23°/0°; (3) α -phenylpropylene, $\text{CHPh}\cdot\text{CHMe}$, which boils at 172—175° and has the sp. gr. 0.93591 at 0°/0° and 0.90902 at 23°/0° (compare Wagner, *J. Russ. Phys. Chem. Soc.*, 1884, **16**, 324).

It is found that α -phenylpropylene is not a product of the original reaction, but is formed from γ -phenylpropylene by isomeric change effected by the agency of the alkali, a change which is shown to be reversible.

T. H. P.

β -Amino- β -phenylpropionic Acid. THEODOR POSNER (*Ber.*, 1905, **38**, 2719).—An addendum to a paper recently published (this vol., i, 577).

Phenyldihydrothiouracil separates from alcohol in leaflets and melts at 240—242°.

A. McK.

Condensation of Phenacylaniline with certain Chloro-ethers. CONCETTO MASELLI (*Gazzetta*, 1905, **35**, ii, 86—94).—Considering the ease with which the hydrazones of γ -keto-acids give up a molecule of water yielding heterocyclic compounds (compare Ach, *Abstr.*, 1890, 70), the author has attempted, but without success, to arrive at α -triazine derivatives by starting from phenylhydrazine and γ -keto-acids containing a nitrogen atom in their atomic chain.

Phenylphenacylurethane, $\text{CH}_2\text{Bz}\cdot\text{NPh}\cdot\text{CO}_2\text{Et}$, obtained by the interaction of molecular proportions of phenacylaniline and ethyl chlorocarbonate in an anhydrous solvent, crystallises from light petroleum in long, colourless prisms or tufts of small prisms melting at 66°. When heated at about 180° or boiled with an excess of alcoholic potassium hydroxide, phenylphenacylurethane yields: (1) an *isonitrile* and (2) *diphenyloxazolone*, $\text{CH}\begin{smallmatrix} \nearrow \text{CPh}\cdot\text{O} \\ \searrow \text{NPh}\cdot\text{CO} \end{smallmatrix}$, which crystallises from benzene in white, shining needles melting at 171°.

Phenylphenacyloxamethane, $\text{CH}_2\text{Bz}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, prepared from phenacylaniline and ethyl chloro-oxalate, crystallises from light petroleum in white, silky prisms melting at 90°. When heated at

about 200°, it yields a *lactone*, which crystallises from benzene in yellow prisms, melting and decomposing at 205°. T. H. P.

Claisen's Cinnamic Acid Synthesis. RICHARD STOERMER and OTTO KIPPE (*Ber.*, 1905, **38**, 3032—3036. Compare this vol., i, 526; Michael, *ibid.*, i, 646).—Claisen's synthesis of cinnamic acid (*Abstr.*, 1890, 891) has been repeated, using ten times the theoretical amount of ethyl acetate. The brown salt formed was removed and washed with dry ether, care being taken to exclude moisture. The filtrate contains ethyl cinnamate in quantity equal to that obtained by Claisen when dilute acid was employed. The solid salt consists of 80 per cent. of sodium acetate together with sodium cinnamate and resinous substances. These facts cannot be reconciled with Michael's view that a salt $\text{ONa}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ is formed, which is decomposed subsequently by water into sodium hydroxide and ethyl cinnamate. The elimination of sodium hydroxide must occur during the condensation and before water is added.

Similar results have been obtained in the synthesis of ethyl phenoxy-cinnamate. Similarly, when sodium reacts with a dry ethereal solution of ethyl β -hydroxy- α -phenoxy-cinnamate, a white salt is formed, and the ethereal solution contains pure ethyl phenoxy-cinnamate. When only the theoretical amount of ethyl acetate is used in the ethyl cinnamate synthesis, considerable amounts of sodium cinnamate are formed due to the hydrolysing action of the sodium hydroxide liberated. J. J. S.

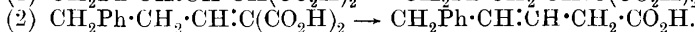
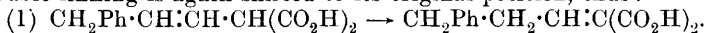
Formation of Isomeric Hydrocinnamylideneacetic Acids. C. N. RIBBER (*Ber.*, 1905, **38**, 2742—2748. Compare *Abstr.*, 1904, i, 894).—Cinnamylideneacetic acid is obtained in good yield when cinnamylidenemalonic acid is sublimed under 0.3 mm. pressure.

$\alpha\delta$ -Dihydrocinnamylideneacetic acid is readily obtained by distilling $\alpha\delta$ -dihydrocinnamylidenemalonic acid at 0.15 mm. pressure, when it boils at 127—128°; it melts at 31°. When its methyl ester is oxidised, a mixture of phenylacetic, benzoic, and malonic acids is formed.

$\gamma\delta$ -Dihydrocinnamylideneacetic acid forms oxalic and hydrocinnamic acids when oxidised by alkaline permanganate.

When $\gamma\delta$ -dihydrocinnamylidenemalonic acid is heated under diminished pressure, $\alpha\delta$ -dihydrocinnamylideneacetic acid is formed, and not the $\gamma\delta$ -acid.

When $\alpha\delta$ -dihydrocinnamylidenemalonic acid is boiled with water or benzene, the double linking is shifted towards the carboxyl group, so that the $\gamma\delta$ -dihydromalonic acid is formed, and when this is heated the double linking is again shifted to its original position, thus:

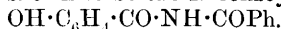


As products of the action of sodium hydroxide on $\alpha\delta$ -dihydrocinnamylideneacetic acid, the author has isolated $\gamma\delta$ -dihydrocinnamylideneacetic acid, β -hydroxyphenylvaleric acid, $\alpha\beta$ -dihydrocinnamylideneacetic acid, and an unsaturated acid, $\text{C}_{11}\text{H}_{12}\text{O}_2$, which is possibly an isomeric

$\alpha\delta$ -dihydro-acid. When $\alpha\beta$ -dihydrocinnamylideneacetic acid is oxidised by alkaline permanganate, benzoic and succinic acids are formed.

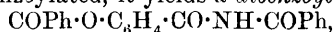
A. McK.

Benzoylation of Salicylamide. ALFRED EINHORN and GUSTAV SCHUPP (*Ber.*, 1905, **38**, 2792—2798. Compare Limpricht, *Annalen*, 1856, **99**, 249).—Gerhardt and Chiozza's (*Jahresber.*, 1856, 502) benzoylsalicylamide is shown to be the *N*-benzoyl derivative,

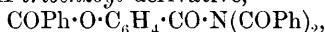


The same benzoyl derivative is obtained by the action of methyl salicylate on the sodium derivative of benzamide (Titherley, *Trans.*, 1902, **81**, 1520, gives the melting point 122° ; this should be 200 — 202°) or by benzoylating salicylamide in pyridine solution.

When further benzoylated, it yields a *dibenzoyl* derivative,

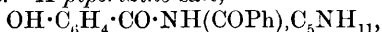


which dissolves in most organic solvents with the exception of ether, crystallises from alcohol in small needles melting at 126 — 128° , gives no coloration with ferric chloride, is insoluble in dilute hydrochloric acid, and is decomposed by potassium hydroxide, both benzoyl groups being eliminated. A *tribenzoyl* derivative,



is obtained when the dibenzoyl compound is carefully benzoylated by the Schotten-Baumann method. It crystallises from hot alcohol or xylene in prismatic needles, melts at 182 — 184° , gives no colour reaction with ferric chloride, and is insoluble in dilute acids or alkalis. When heated with pyridine, it yields *N*-benzoylsalicylamide, or with potassium hydroxide, salicylamide and benzoic acid.

N-Benzoylsalicylamide forms an *additive compound* with its sodio-derivative (Limpricht), namely, $\text{C}_{28}\text{H}_{21}\text{O}_6\text{N}_2\text{Na}$, which crystallises from alcohol in golden-yellow needles. The same compound is formed when carbon dioxide is passed into a solution of benzoylsalicylamide in sodium hydroxide. A *piperidine* salt,



is obtained by the addition of piperidine to an alcoholic solution of the benzoyl derivative. It crystallises in yellow needles and melts at 145 — 147° . It forms a colourless additive product with *N*-benzoylsalicylamide, probably

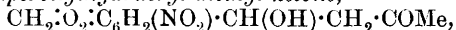


which melts at 153 — 155° .

J. J. S.

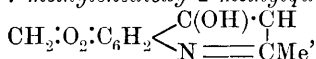
By-products from the Preparation of Piperonalindigo and its Oxidation. PAUL HERZ (*Ber.*, 1905, **38**, 2853—2860. Compare Book, *Abstr.*, 1902, i, 464; 1903, i, 653).—The following four substances are obtained as by-products from the preparation of bis-methylenedioxyindigo (piperonalindigo) (Liebermann and Haber, *Abstr.*, 1890, 1140):

(1) *o*-Nitropiperonylhydracryl methyl ketone,



which represents the first stage in the formation of piperonalindigo from nitropiperonal and acetone, crystallises in long, yellow plates,

melts at 145° , forms piperonalindigo when treated with sodium hydroxide, and when boiled with acetic anhydride yields *o*-nitropiperonylacryl methyl ketone. The *phenylhydrazone*, $C_{17}H_{17}O_3N_3$, crystallises in yellow leaflets and melts and decomposes at $134-139^{\circ}$. The *oxime*, $C_{11}H_{12}O_6N_2 \cdot H_2O$, crystallises in yellow needles, melts at $78-83^{\circ}$, loses H_2O in the desiccator or at 100° , and when anhydrous melts at 130° . 4-Hydroxy-6:7-methylenedioxy-2-methylquinoline,



formed by reduction of *o*-nitropiperonylhydracryl methyl ketone with zinc dust in boiling aqueous solution, crystallises in white needles and melts at 185° . The *hydrochloride*, $C_{11}H_9O_3N \cdot HCl$, crystallises in silky needles and melts at $230-235^{\circ}$ with decomposition; the *platini-chloride*, $(C_{11}H_9O_3N)_2 \cdot H_2PtCl_6$, forms orange needles and melts at 234° ; the *acetyl* derivative, $C_{13}H_{11}O_4N$, crystallises in colourless needles and melts at 110° .

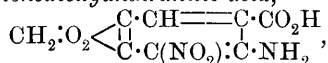
(2) *o*-Nitropiperonylacryl methyl ketone (Haber, Abstr., 1891, 705) forms an *oxime*, $C_{11}H_{10}O_5N_2$, which crystallises in yellow leaflets and melts and decomposes at 220° .

(3) *Di-o-nitrodipiperonylhydracryl ketone*,
 $[CH_2:O_2:C_6H_2(NO_2) \cdot CH(OH) \cdot CH_2]_2CO$,
 crystallises in colourless needles, melts at 195° , is insoluble in boiling water, but moderately soluble in alcohol or acetone, and when boiled with acetic anhydride yields di-*o*-nitrodipiperonylacryl ketone (Haber, *loc. cit.*).

(4) Nitromethylenecatechol (Jobst and Hesse, Abstr., 1878, 1733) is obtained from the crude product from the interaction of nitropiperonal and acetone by sublimation.

5:6-Methylenedioxyisatin, $CH_2:O_2:C_6H_2 \begin{array}{l} \diagup CO \\ \diagdown N \end{array} > C \cdot OH$, formed by warming piperonalindigo with dilute nitric acid, crystallises in dark red needles, melts and decomposes at 280° , dissolves in concentrated sulphuric acid to form a blue solution, from which it is precipitated in needles on adding water, and with thiophen and sulphuric acid forms *dioxymethyleneindophenin*, $C_{13}H_7O_3NS$, as a blue precipitate.

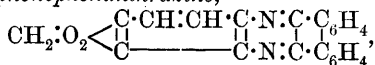
3-Nitro-4:5-methylenedioxyanthranilic acid,



formed by the action of nitric acid on piperonalindigo, crystallises in yellow needles, forms aqueous and alcoholic solutions with green fluorescence, and when warmed in alkaline solution loses carbon dioxide

and yields *nitroaminomethylenecatechol*, $CH_2:O_2 \begin{array}{l} \diagup C \cdot CH = CH \\ \diagdown C \cdot C(NO_2) \cdot C \cdot NH_2 \end{array}$

This crystallises in orange leaflets, melts at 195° , is soluble in hot water or hydrochloric acid, and is precipitated from its concentrated solution in concentrated hydrochloric acid on addition of water. When reduced with zinc dust in boiling aqueous solution, this forms *diaminomethylenecatechol*, which in solution gives the reactions for ortho-diamines and on oxidation yields a yellow, sparingly soluble *base*, which behaves as a diaminophenazine.

Methylenedioxyphenophenanthrazine,

is formed by reduction of nitroaminomethylenecatechol with zinc dust in alcoholic glacial acetic acid solution, and addition of phenanthraquinone to the diamine solution so formed. It crystallises in yellow needles, melts at 309°, dissolves easily in glacial acetic acid, but only sparingly in alcohol, to form violet, fluorescent solutions, and forms a reddish-violet solution in concentrated sulphuric acid.

G. Y.

Phenyl Ether-*o*-carboxylic [Aryloxybenzoic] Acids. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 158998. Compare Abstr., 1904, i, 499).—Sodium phenoxide, or the alkali derivatives of other phenols, reacts readily with *o*-chlorobenzoic acid in presence of copper or copper salts to form *o*-carboxylic acids of the corresponding phenyl ether.

o-Tolyloxybenzoic acid separates from a mixture of benzene and light petroleum in coarse crystals and melts at 130°; *p*-tolylloxybenzoic acid forms large crystals and melts at 117°; *β*-naphthylloxybenzoic acid forms colourless crystals and melts at 121°. The acids are insoluble in water, and dissolve readily in alcohol or benzene.

C. H. D.

Enantiomorphism of the cycloPropanecarboxylic Acids. EDUARD BUCHNER and RICHARD VON DER HEIDE (*Ber.*, 1905, 38, 3112—3119).—*r*-trans-cycloPropane-1:2-dicarboxylic acid can be resolved into its optically active components by means of brucine, quinine, or cinchonidine in aqueous solution.

The *d*-acid, $\text{C}_5\text{H}_6\text{O}_4$, melts at 175°, and has $[\alpha]_D + 84.42$ — 84.87° at 26°. Its *brucine* salt, $2\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}_2 \cdot \text{C}_5\text{H}_6\text{O}_4 \cdot 6\text{H}_2\text{O}$, crystallises slowly from the cold aqueous solution and loses $6\text{H}_2\text{O}$ at 120°; the *acid-quinine* salt, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot \text{C}_5\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$, crystallises from the cold aqueous solution in stellate aggregates of hexagonal crystals and loses $2\text{H}_2\text{O}$ at 125°; the *cinchonidine* salt is soluble in cold water.

The *l*-acid melts at 175° and has $[\alpha]_D - 84.40$ — 84.53° at 27°. Its *cinchonidine* salt, $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot \text{C}_5\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$, crystallises from the aqueous solution on cooling and loses $2\text{H}_2\text{O}$ at 125°; the *brucine* and *quinine* salts are soluble in cold water.

r-cycloPropane-1:1:2-tricarboxylic acid can be resolved into its active components in the same manner as *r*-trans-cyclopropane-1:2-dicarboxylic acid. The *d*-acid decomposes at 187° and has $[\alpha]_D + 84.57^\circ$ at 26°. The *brucine* salt, $\text{C}_{53}\text{H}_{58}\text{O}_{14}\text{N}_4 \cdot 4\text{H}_2\text{O}$, loses $4\text{H}_2\text{O}$ at 130°; the *quinine* salt, $\text{C}_{46}\text{H}_{54}\text{O}_{10}\text{N}_4 \cdot 2\text{H}_2\text{O}$, loses $2\text{H}_2\text{O}$ at 130°. The *l*-acid has $[\alpha]_D - 84.65^\circ$ at 26°; the *cinchonidine* salt, $\text{C}_{25}\text{H}_{28}\text{O}_7\text{N}_2$, is anhydrous at 130°.

cis-cycloPropane-1:2- and cyclopropane-1:1-dicarboxylic and *cis*-trans-cyclopropane-1:2:3-tricarboxylic acids cannot be resolved into optically active components.

cis-cycloPropane-1:2:3-tricarboxylic acid was not investigated.

G. Y.

Condensation of Benzil with Resorcinol. I. Non-fluorescent Substances. HANS VON LIEBIG (*J. pr. Chem.*, 1905, [ii], 72, 105—172. Compare Abstr., 1899, i, 915; 1903, i, 828, 829).—Benzil, resorcinol, and sodium sulphate are heated together at 180—200° for 7—8 hours, and the cooled product washed and treated with aqueous potassium hydroxide. After being washed with hydrochloric acid and water, the undissolved portion of the product, on treatment with alcohol, yields 4-hydroxy-2-ethoxytritanic anhydride, 2:4-dihydroxytritanolactone, 3:5-dihydroxytritanolactone, a compound, $C_{40}H_{28}O_5$, which is obtained as a sandy-red powder, and the anhydride of this, $C_{40}H_{26}O_4$, which forms a yellowish-brown or red powder. On extraction with ether, the aqueous alkaline solution yields resorcinolbenzein, 3:5-dihydroxytritanic acid and its lactone, 3:5-dihydroxytritanic lactone ether, 4-hydroxy-2-ethoxytritanic anhydride, and two substances which are probably identical with Barth and Weidel's resorcinylic ethers, $C_{12}H_{10}O_3$ and $C_{24}H_{18}O_8$ (Abstr., 1878, 61).

The name tritanic acid is used in place of triphenylmethanecarboxylic (triphenylacetic) acid.

2:4-Dihydroxytritanolactone,
$$\begin{array}{c} \text{CPh}_2 \cdot \text{C} \cdot \text{C}(\text{OH}) : \text{C} \\ | \quad | \\ \text{CO} \cdot \text{O} \cdot \text{C} - \text{CH} - \text{C} \cdot \text{OH} \end{array}$$
 crystallises

from benzene in small, rhombic leaflets containing benzene of crystallisation, melts at 264°, is slightly less soluble than 3:5-dihydroxytritanolactone, and dissolves in alcohol to form a solution which on exposure to air becomes green and finally a dirty brown.

3:5-Dihydroxytritanic acid, $C_6H_3(\text{OH})_2 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$, crystallises in flocculent aggregates of needles on addition of acetic acid to the aqueous solution of its tripotassium salt; it melts with effervescence in a capillary tube at 120—130°, and changes into the lactone slowly at the ordinary temperature, more quickly on the water-bath, or immediately at 120°. The acid crystallises from its ethereal and alcoholic solutions in rhombohedra containing ether and alcohol respectively of crystallisation. The stability of this acid is in agreement with the positions 3 and 5 assigned to the hydroxyl groups. The sodium salt, $C_{20}H_{15}O_4Na \cdot 2H_2O$, crystallises in small clusters of needles or hexagonal prisms; the potassium salt, $C_{20}H_{15}O_4K \cdot 2H_2O$, crystallises in long, slender needles; $C_{20}H_{15}O_4K \cdot C_2H_6O$ crystallises in rectangular plates; the ammonium, $C_{20}H_{15}O_4NH_4 \cdot H_2O$, the trisodium,

$C_{20}H_{13}O_4Na_3 \cdot C_2H_6O \cdot 4H_2O$ or $C_{20}H_{13}O_4Na_3 \cdot 4\frac{1}{2}H_2O$, and tripotassium, $C_{20}H_{13}O_4K_3 \cdot CH_4O \cdot 4H_2O$, salts are described. The lactone crystallises from benzene in colourless leaflets, or from alcohol in large, monoclinic rhombohedra, and decomposes with formation of diphenylmethane when heated under the atmospheric pressure, but distils partly unchanged in a vacuum. It is precipitated from its boiling alcoholic solution by a current of hydrogen chloride, gives with concentrated sulphuric acid a yellow coloration which gradually becomes red, and dissolves in aqueous alkali hydroxides to form solutions which become brown on exposure to air. The substance melting at 120°, and previously supposed to be the monoacetyl derivative (Abstr., 1903, i, 828), is now found to be a mixture of the lactone and its acetyl derivative, $C_{20}H_{14}O_2Ac$, which

melts at 161° and was termed previously the diacetyl derivative. The supposed dibenzoyl derivative has the formula $C_{20}H_{14}O_3Bz$.

Methyl 3:5-dimethoxytritanate, $C_6H_3(OMe)_2 \cdot CPh_2 \cdot CO_2Me$, formed by the action of warm methyl sulphate on 3:5-dihydroxytritanic lactone in warm aqueous potassium hydroxide solution, crystallises in glistening, rhombic leaflets, melts at 168° , gives a blood-red coloration with sulphuric acid, and is only partly hydrolysed by prolonged boiling with alcoholic potassium hydroxide or by treatment with fused potassium hydroxide at 150° , with formation of the corresponding dimethoxy-acid.

The action of methyl sulphate on 3:5-dihydroxytritanolactone in aqueous alkali hydroxide solution at the ordinary temperature leads to the formation of 3:5-dimethoxytritanic acid and of 5-methoxy-3-hydroxytritanolactone.

3:5-Dimethoxytritanic acid, $C_{22}H_{20}O_4$, crystallises in four-sided prisms, melts at 246° , decomposes and evolves gas at 300° , gives a blood-red coloration with sulphuric acid, and forms its methyl ester when shaken with methyl sulphate and aqueous potassium hydroxide. The *sodium* salt (with $2H_2O$) crystallises in long, slender needles; the *potassium* salt, $C_{22}H_{19}O_4K \cdot 2H_2O$, forms long, spicular needles; the *ammonium* salt (with $2H_2O$) crystallises in clusters of short, slender needles. The *barium*, *copper*, and *silver* salts are described.

The action of boiling acetyl chloride on the dimethoxy-acid leads to the formation of *3-hydroxy-5-methoxytritanolactone*, $C_{21}H_{16}O_3$, which crystallises in long rhombohedra, melts at $180-181^{\circ}$, is almost insoluble in aqueous potassium hydroxide on the water-bath, but dissolves on boiling to form a solution from which, on acidification, *3-hydroxy-5-methoxytritanic acid* is precipitated; this, when heated on the water-bath, is reconverted into the lactone.

The action of ethyl sulphate on 3:5-dihydroxytritanolactone in aqueous alkali hydroxide solution leads to the formation of 3:5-diethoxytritanic acid and its ethyl ester and hydroxyethoxytritanolactone.

3:5-Diethoxytritanic acid, $C_6H_3(OEt)_2 \cdot CPh_2 \cdot CO_2H$, crystallises in small, rectangular leaflets and melts at $181-182^{\circ}$. The *ethyl* ester, $C_{36}H_{28}O_4$, crystallises in slender, white needles, melts at 122° , and gives a red coloration with sulphuric acid, but more slowly than the corresponding methyl derivative. *3-Hydroxy-5-ethoxytritanolactone*, $C_{22}H_{18}O_3$, crystallises in rhombic leaflets and melts at $151-152^{\circ}$.

When tripotassium 3:5-dihydroxytritanate is heated for eight hours on the water-bath and the product treated with water and hydrochloric acid, there is obtained a *substance*, $C_{40}H_{30}O_7$, as a yellowish-brown powder, which is formed also by the action of a current of air on the alkaline solution of the acid. The action of fused potassium hydroxide on 3:5-dihydroxytritanolactone leads to the formation of diphenylmethane, resorcinol, resoreylic and benzoic acids, and a *substance*, $C_{28}H_{30}O_4$, which is formed also when the tripotassium salt is heated at 240° . This sinters and decomposes at about 160° , and dissolves in alcoholic potassium hydroxide, forming a brownish-red solution with intense green fluorescence.

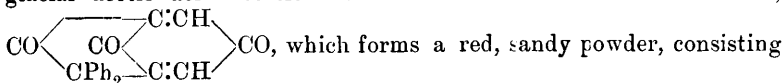
When heated at 300° , potassium 3:5-dihydroxytritanate yields (1)

a small amount of diphenylmethane, (2) the phenol *ether* of 3:5-dihydroxytritanol, $O\left[\begin{array}{c} \text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH} \\ | \quad | \\ \text{C}\cdot\text{CH}=\text{C}\cdot\text{CPh}_2\cdot\text{OH} \end{array}\right]_2$, which dissolves in water

to form a blue fluorescent liquid, in aqueous ammonia or alkali hydroxides or carbonates to form brownish-red solutions with slight blue fluorescence, which becomes green on addition of alcohol, and (3) 3:5-dihydroxytritanol *ether*, $O[\text{C}_6\text{H}_3(\text{OH})\cdot\text{CHPh}_2]_2$, which is insoluble in water but dissolves in alcohol or aqueous alkali hydroxides to form solutions with green fluorescence, which becomes blue on dilution with water.

If 3:5-dihydroxytritanolactone is warmed with concentrated sulphuric acid and the product treated with ammonium sulphate, there is formed the *ammonium sulphate*, $\text{C}_{20}\text{H}_{13}\text{O}_3\cdot\text{SO}_3\text{NH}_4\cdot\frac{1}{2}\text{H}_2\text{O}$, which crystallises from water in spicular needles, or from alcohol with alcohol of crystallisation, melts when anhydrous at $224\text{--}225^\circ$, and gives a reddish-violet coloration with aqueous ferric chloride.

Oxidation of 3:5-dihydroxytritanolactone with lead peroxide in glacial acetic acid solution leads to the formation of a *substance*,



of microscopic, spherical crystals, which melts above 290° . Oxidation of the lactone with chromic acid in glacial acetic acid solution leads to the formation of benzophenone, or with alkaline permanganate to the formation of benzophenone and a number of intermediate products.

Diphenylmethane was obtained by the distillation of 3:5-dihydroxytritanolactone.

3:5-Dihydroxytritanolactone *ether*, $O(\text{C}_{20}\text{H}_{13}\text{O}_2)_2$, crystallises in rhombic or hexagonal leaflets, melts at 224° , gives a blood-red coloration with concentrated sulphuric acid, and when distilled is decomposed with formation of diphenylmethane and a *substance* which dissolves in benzene to form a reddish-brown solution with green fluorescence. The *sodium* salt, $O(\text{C}_{20}\text{H}_{13}\text{O}_3\text{Na})_2$, which forms glistening needles, and the *potassium* salt, $O(\text{C}_{20}\text{H}_{13}\text{O}_3\text{K})_2$, were analysed. The *ether* of methyl 3:5-dimethoxytritanate, $O[\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CPh}_2\cdot\text{CO}_2\text{Me}]_2$, formed by the action of methyl sulphate and aqueous potassium hydroxide on the potassium salt, crystallises in spicular needles, melts at 176° , and gives a blood-red coloration with concentrated sulphuric acid. Together with the ester there is formed a *substance* which melts at 91° , decomposes and evolves gas at 150° , and is more soluble in alcohol.

The *ether* of 3:5-dimethoxytritanic acid, $O[\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}]_2$, is formed by the hydrolysis of its ester by means of potassium hydroxide or by the action of methyl sulphate on potassium dihydroxytritanate ether in presence of an excess of potassium hydroxide. It crystallises in small, spicular needles and melts and decomposes at 274° , or sometimes at 304° .

G. Y.

Condensation of α -Keto-acids with Aldehydes by means of Hydrochloric Acid or Sodium Hydroxide. EMIL ERLENMEYER, jun. (*Ber.*, 1905, 38, 3119—3125. Compare Abstr., 1903, i,

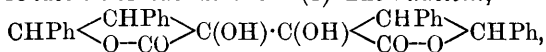
698).—Phenylpyruvic acid and benzaldehyde condense with sodium hydroxide in aqueous solution to form *sodium γ -hydroxy- α -keto- β - γ -diphenylbutyrate*, which separates slowly in colourless crystals, and on addition of hydrochloric acid yields the free *acid*,

$$\text{OH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CO}_2\text{H}.$$

This separates from alcohol in glistening crystals, melts at 175° , is soluble in ether, and has a strong acid reaction. When warmed with an excess of aqueous sodium hydroxide, it decomposes with formation of benzaldehyde, and when warmed with hydrochloric acid is converted into α -keto- β - γ -diphenylbutyrolactone, melting at 206° . The α -keto-acid forms with hydroxylamine an amorphous *oxime* melting at 96° , and with phenylhydrazine the *phenylhydrazone*, $\text{NHPh}\cdot\text{N}\cdot\text{C} \begin{smallmatrix} \text{CHPh}\cdot\text{CHPh} \\ \text{CO}-\text{O} \end{smallmatrix}$, melting at 188° . With phenylhydrazine, α -keto- β - γ -diphenylbutyrolactone forms a *phenylhydrazine* salt, $\text{C}_{22}\text{H}_{20}\text{O}_3\text{N}_2$, melting at 136° .

Reduction of γ -hydroxy- α -keto- β - γ -diphenylbutyric acid with sodium amalgam leads to the formation of an α -hydroxy- β - γ -diphenylbutyrolactone, which separates from chloroform on addition of light petroleum as a microcrystalline powder and melts at 127° , and of an *isomeride* which crystallises from alcohol in small needles, melts at 171° , and is insoluble in chloroform. Both these products yield desylacetic acid when boiled with dilute hydrochloric acid; together with the two products melting at 127° and 170° obtained by Erlenmeyer and Lux (Abstr., 1898, i, 668) by reduction of α -keto- β - γ -diphenylbutyrolactone, with which they are not identical; they form two pairs of stereoisomerides and all the four possible racemic modifications of α -hydroxy- β - γ -diphenylbutyrolactone are now known. The melting points of a number of stereoisomeric racemic α -hydroxybutyrolactones are given to show that close agreement of the melting points of the pairs of stereoisomerides is not uncommon.

When treated with concentrated sodium hydroxide, α -keto- β - γ -diphenylbutyrolactone is hydrolysed to the γ -hydroxy-acid melting at 175° ; this, on reduction with sodium amalgam in concentrated solution, yields phenyl- α -lactic acid and two products which are not obtained by reduction of the lactone. (1) The *dilactone*,



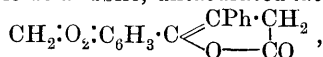
crystallises in transparent prisms, melts at 236° , has a neutral reaction, and forms a sparingly soluble *barium* salt. (2) *s*-Dibenzyltartaric acid, $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})(\text{CH}_2\text{Ph})\cdot\text{C}(\text{OH})(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$, crystallises from chloroform, melts at 212° , is soluble in sodium hydrogen carbonate solution, and forms a sparingly soluble *barium* salt; the *potassium* and *silver* salts were analysed. As this acid is formed only in small quantity by reduction of phenylpyruvic acid by means of sodium amalgam in concentrated solution, but in large quantity by reduction with zinc and hydrochloric acid, it is formed probably by decomposition of a reduction product of γ -hydroxy- α -keto- β - γ -diphenylbutyric acid. The condensation of benzaldehyde and pyruvic acid in presence of sodium hydroxide or hydrochloric acid leads to the formation of two stereoisomeric cinnamylformic acids. Erlenmeyer and Stirr's solid acid forms a crystalline *phenylhydrazone* melting at

162°, and is converted by concentrated hydrochloric acid into Claisen and Claparède's oily acid (Abstr., 1882, 520). This forms an amorphous *phenylhydrazone*, $C_{16}H_{14}O_2N_2$, melting at 94°, and on reduction yields an amorphous *α-hydroxyphenylisocrotonic acid*, $C_{16}H_{10}O_3$?, which is converted by boiling hydrochloric acid into benzoylpropionic acid. When dissolved in aqueous sodium hydroxide, Claisen and Claparède's oily acid is slowly converted into the sodium salt of Erlenmeyer and Stirr's solid acid. G. Y.

Preparation of αβ- and βγ-Unsaturated Lactones. EMIL ERLIENMEYER, jun. (*Ber.*, 1905, 38, 3125—3129. Compare Abstr., 1904, i, 892; Thiele, Abstr., 1899, i, 216).—The unsaturated *acid*, $OMe \cdot C_6H_4 \cdot CH : CPh \cdot CH(OH) \cdot CO_2H$, is formed by boiling α-oxy-β-phenyl-γ-methoxyphenylbutyrolactone with zinc dust in glacial acetic acid solution for three hours; it crystallises from chloroform and light petroleum in slender needles, melts at 126°, and when dissolved in acetic anhydride containing a small quantity of sulphuric acid and the mixture poured into water yields the labile, unsaturated lactone melting at 105°. The substance obtained previously (Erlenmeyer and Lattermann, Abstr., 1904, i, 1017), which melted at 145° and was supposed to be the βγ-unsaturated α-hydroxy-acid, was impure γ-keto-acid. When similarly reduced, the γ-keto-acid yields the stable, unsaturated lactone melting at 122°.

When treated with sulphuric acid and acetic anhydride, γ-oxy-β-phenyl-γ-isopropylphenylbutyric acid, melting at 111° (Erlenmeyer and Kehren, Abstr., 1904, i, 1015), yields a labile, unsaturated Δ²-lactone, $C_{19}H_{18}O_2$, which separates from alcohol in stout crystals, melts at 122°, and easily changes into the stable, unsaturated Δ¹-lactone melting at 124°. Both lactones yield the same condensation product with benzaldehyde in presence of piperidine.

When treated with acetic anhydride and sulphuric acid, Erlenmeyer and Braun's βγ-unsaturated α-hydroxy-acid (Abstr., 1904, i, 1016) yields the stable lactone melting at 183°, which has, therefore, the ethylene linking in the αβ-position. The γ-keto-acid obtained on hydrolysis of the stable lactone on treatment with acetic anhydride and sulphuric acid yields a labile, unsaturated *lactone*,

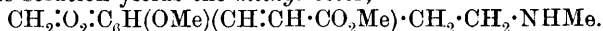


which by piperidine in alcoholic solution is converted into the stable lactone (m. p. 183°). Both lactones yield a condensation product with benzaldehyde, melting at 196°.

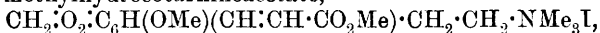
These facts support the author's view that an αβ-unsaturated lactone forms the intermediate product in the formation of γ-keto-acids from βγ-unsaturated α-hydroxy-acids. G. Y.

Acetylhydrocotarnineacetic Acid. WILHELM AHLERS (*Ber.*, 1905, 38, 2873—2877. Compare Bowman, Abstr., 1887, 1056. Liebermann and Kropf, Abstr., 1904, i, 263).—*Hydrocotarnineacetic acid*, $CH_2 : O_2 \cdot C_6H(OMe)(CH : CH \cdot CO_2H) \cdot CH_2 \cdot CH_2 \cdot NHMe$, prepared by the action of silver oxide on the hydrochloride (Bowman), is obtained in the crystalline state on evaporating the aqueous solution;

it melts at 116° , and when treated with hydrogen chloride in methyl alcoholic solution yields the *methyl* ester,

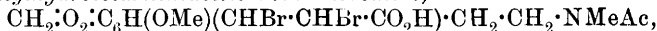


This crystallises from methyl alcohol and melts at 63° ; the *platini-chloride*, $(\text{C}_{15}\text{H}_{19}\text{O}_5\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, forms a yellow, flocculent precipitate and decomposes, without melting, at 90° . The action of methyl iodide on the methyl ester leads to the formation of the *methiodide* of methyl methylhydrocotarnineacetate,



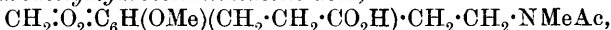
which forms yellow crystals and melts at 119° .

Acetylhydrocotarnineacetic acid dibromide,



formed by the action of bromine on the acid in glacial acetic acid solution, separates from alcohol in glistening, white crystals, melts at 188° , and is soluble in aqueous sodium carbonate. The *methyl* ester, $\text{C}_{17}\text{H}_{21}\text{O}_6\text{NBr}_2$, crystallises from aqueous methyl alcohol and melts at 121° .

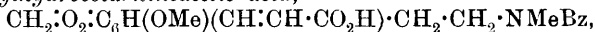
Dihydroacetylhydrocotarnineacetic acid,



formed by reduction of acetylhydrocotarnineacetic acid with sodium amalgam, melts at 176° and decolorises potassium permanganate only slowly.

Acetylcotarnine, $\text{CH}_3\cdot\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})(\text{CHO})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMeAc}$, is formed by the action of potassium permanganate on acetylhydrocotarnineacetic acid dissolved in aqueous sodium carbonate or by the action of a small quantity of acetic anhydride on cotarnine. It crystallises from alcohol and melts at 146° , and yields acetylcotarnineacetic acid when heated with sodium acetate and acetic anhydride at $100\text{--}120^{\circ}$ in a sealed tube. The *oxime*, $\text{C}_{14}\text{H}_{13}\text{O}_5\text{N}_2$, melts at 156° .

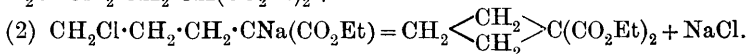
Benzoylhydrocotarnineacetic acid,



formed by heating benzoylcotarnine with acetic anhydride and sodium acetate, crystallises in needles. The *ethyl* ester melts at 81° ; the *silver* salt, $\text{C}_{21}\text{H}_{20}\text{O}_6\text{NAg}$, is obtained as a white precipitate. G. Y.

Preparation of Ethyl Tetramethylene-1:1-dicarboxylate.

NIC. M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 507—509).—When Perkin's method is applied to the preparation of ethyl *cyclo*-butane-1:1-dicarboxylate, from ethyl sodiomalonate (2 mols.) and $\alpha\gamma$ -dibromopropane (1 mol.), poor yields are obtained and the ester is difficult to separate. Much better results are obtained by the interaction of ethyl sodiomalonate and α -chloro- γ -bromopropane, the reactions being represented by (1) $\text{CHNa}(\text{CO}_2\text{Et})_2 + \text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl} = \text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2 + \text{NaBr}$ and



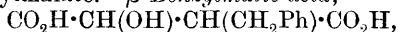
Prepared in this way, the ester is easily separated and boils at $222\text{--}226^{\circ}$. T. H. P.

β -Benzylmalic Acid. OSCAR DOEBNER and M. KERSTEN (*Ber.*, 1905, 38, 2737—2742).—The method of preparation of β -benzylmalic

acid is analogous to that of ethylmalic acid (this vol., i, 737). Ethyl benzylmalonate was prepared according to Fittig and Röder's method by boiling together ethyl malonate, sodium ethoxide, and benzyl chloride in ethyl-alcoholic solution. Benzylmalonic acid, prepared by hydrolysing it, melts at 117°.

γ -Trichloro- β -hydroxy- α -benzylbutyric acid, prepared by heating benzylmalonic acid with chloral and pyridine for six hours at 60–70°, separates from a mixture of ethyl alcohol and water in glistening leaflets and melts at 182°. Its *silver*, *lead*, and *copper* salts were examined.

When heated with a 10 per cent. aqueous solution of potassium hydroxide, γ -trichloro- β -hydroxy- α -benzylbutyric acid is converted into potassium β -benzylmalate. β -Benzylmalic acid,



separates from a mixture of ether and light petroleum in tiny crystals and melts at 155°. Its *silver*, *lead*, *copper*, *barium*, and *strontium* salts are described.

Phenylitaconic acid is produced when β -benzylmalic acid is heated at 200°, whilst phenyleitraconic acid is formed probably as an intermediate product.

A. McK.

Action of Ethyl Sodiomalonate on Sodium Salts of Unsaturated Acids. GUSTAV REINICKE (*Annalen*, 1905, 341, 80–98. Compare preceding abstract).—When the sodium salt of β -benzylidenelævulic acid is treated with ethyl sodiomalonate, a hydroresorcinol derivative, *carbethoxyphenylhydroresorcinyllactic acid*, $\text{CH}(\text{CO}_2\text{Et})\cdot\text{CHPh}$
 $\text{CO}—\text{CH}:\text{C}(\text{OH}) > \text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is formed. The acid crystallises from boiling water in aggregates melting at 167°, and from dilute alcohol in rhombohedra melting at 156°; with alcoholic ferric chloride it gives a violet coloration. Methyl sodiomalonate yields an analogous acid, $\text{C}_{16}\text{H}_{16}\text{O}_6$, which crystallises in leaflets melting at 172–173°; the sodium salt, $\text{C}_{16}\text{H}_{14}\text{O}_6\text{Na}_2$, was prepared.

From δ -benzylidenelævulic acid and ethyl sodiomalonate, the isomeric acid, $\text{CHPh}\cdot\text{CH}_2\cdot\text{C}(\text{OH}) > \text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained, crystallising from water in needles with H_2O , melting at about 123°; when heated at 100°, it loses water and then melts at 143°.

Addition does not take place between sodium benzylidenemalonate and ethyl sodiomalonate. The *monoethyl* ester of benzylidenemalononic acid, $\text{CHPh}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CO}_2\text{H}$, is formed by heating an acetic acid solution of potassium ethyl malonate and benzaldehyde, and crystallises in prismatic plates melting at 85°. It forms an additive compound with ethyl sodiomalonate, but not with sodium ethoxide.

Ethyl cinnamate forms an additive product with potassium ethyl malonate in the presence of sodium ethoxide, but not with sodium malonate under the same conditions.

Cinnamoyl-o-aminobenzoic acid, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, prepared by heating cinnamoyl chloride and anthranilic acid, forms crystals melting at 192°; at the same time, a neutral compound crystal-

lising in needles and melting and decomposing at $226-228^{\circ}$ is produced. *Cinnamoyl-m-aminobenzoic acid* forms rhombohedra melting at 253° , and the corresponding *p-acid* crystals melting and decomposing at 282° . An additive product with ethyl sodiomalonate is only obtained from the ortho-acid.

K. J. P. O.

Fluorescein and the Non-existence of β -*p*-Dibromodinitrobenzene. GUSTAV HELLER and HEINRICH L. MEYER (*J. pr. Chem.*, 1905, [ii], 72, 197—200. Compare Heller, Abstr., 1895, i, 234; Meyer, *ibid.*, i, 538).—That only one dihydroxybenzoylbenzoic and one dibromodihydroxybenzoylbenzoic acid are obtained from fluorescein and eosin respectively shows both hydroxyl groups in these substances to occupy the para-position.

The authors have been able to isolate only α - and γ -*p*-dibromodinitrobenzenes from the product obtained on nitration of *p*-dibromobenzene. The part of the product which should have contained Austen's β -*p*-dibromodinitrobenzene (this Journal, 1876, ii, 406, 513) yielded, on reduction, *p*-dibromo-*o*-diamino- and *p*-dibromo-*p*-diamino-benzene together with a small amount of a substance which was probably *m*-dibromoaniline. Austen's substance may have been γ -compound.

G. Y.

Meconic Acid. L. VALENTI (*Chem. Centr.*, 1905, ii, 491; from *Boll. Chim. Farm.*, 1905, 44, 373—380).—Meconic acid is extracted from powdered opium by evaporating it to dryness with dilute hydrochloric acid, extracting with absolute alcohol, and making the filtrate alkaline by means of alcoholic potash; the precipitate so formed is washed with a mixture of equal parts of alcohol and ether, dissolved in water, and treated with lead acetate; the precipitated lead salt after washing is decomposed with hydrogen sulphide, the solution being boiled, filtered, and cooled. One part of pure meconic acid dissolves in 50 parts of methyl alcohol or ethyl acetate, and in 100 parts of water or acetone; it is soluble in alcohol or benzene, very slightly so in amyl alcohol, light petroleum, carbon disulphide, or glycerol. A number of colour reactions are described which may be obtained under suitable conditions from meconic acid by the action of potassium persulphate, iodic acid, concentrated nitric acid, followed by potassium hydroxide, sodium metavanadate, ammonium molybdate, and ferric chloride. A full account is also given of the precipitation reactions obtained by the addition of albumin, the nitrates of mercury and silver, and by lead acetate and the salts of cobalt, nickel, and gold. Papaverine hydrochloride and quinine sulphate both give white precipitates with ammonium meconate. Apomorphine hydrochloride produces at first a white and then a blue precipitate, and strychnine sulphate gives after some time a crystalline precipitate. Meconic acid reduces potassium dichromate and permanganate in cold acid solution, and potassium ferrocyanide on heating, with the production of a blue coloration.

The salts of meconic acid are prepared by mixing alcoholic solutions of the acid and of the acetate of the corresponding metal, if necessary adding ether to ensure complete precipitation. Meconic acid, $C_5H(OH)_2(CO_2H)_2O_2, 3H_2O$, may be titrated with *N*/10 potassium

hydroxide until the appearance of a yellow colour, which indicates the formation of a basic salt by replacement of a phenolic hydroxyl, the normal salts being colourless. Meconic acid and its salts are not poisonous, although they combine with proteids. Meconic acid can always be detected in toxicological cases by adding ferric chloride to the dried organs after treatment with hydrochloric acid. P. H.

Compounds from Lichens. XIV. WILHELM ZOPF (*Annalen*, 1905, 340, 276—309. Compare Abstr., 1904, i, 1020; this vol., i, 212).—Sphærophorin, sphærophoric acid, fragilin, and a small amount of a violet substance have been obtained from a specimen of *Sphærophorus fragilis* from the Tafelsteinkuppe, near Wolfshan, in the Riesengebirg (compare Abstr., 1898, i, 489). Sphærophorin, $(C_{14}H_{16}O_4)_n$ or $C_{28}H_{34}O_8$, crystallises from benzene in long, slender, white needles, is soluble in ether, and reduces potassium permanganate in cold sodium carbonate solution. Sphærophoric acid crystallises from ether in large, rhombic plates, from glacial acetic acid in thin leaflets resembling thamnolic and squamatic acids, melts and decomposes at 206—207°, and dissolves in aqueous alkali hydroxides or carbonates to form yellow solutions, which become slowly red or violet, and on addition of hydrochloric acid yield a yellow resin and a colourless substance crystallising in sheaves of needles. The acid reddens alcoholic litmus, gives a violet coloration with traces of ferric chloride, reduces potassium permanganate in cold sodium carbonate solution, and dissolves in concentrated sulphuric acid to form a colourless solution, which on warming becomes red, brown, and finally black. With baryta water, sphærophoric acid forms a colourless substance, which crystallises in stellate aggregates of long, slender, feathery needles. Fragilin crystallises in rosettes of rectangular plates, is green by transmitted light, and is insoluble in cold aqueous sodium carbonate, but dissolves when warmed to form a reddish-violet solution.

Biatora mollis (*Lecidea mollis*) contains 4·5 per cent. of diffusin (Abstr., 1899, i, 716; 1903, i, 762), which is now termed *diffusic acid*. This gives a violet coloration with ferric chloride, and when boiled with dilute potassium hydroxide forms a substance which gives a red coloration with bleaching powder, and red with green fluorescence on addition of a drop of chloroform. The sodium and barium salts are described.

Rhizocarpic acid has been found in a sterile specimen of *Biatora lucida* obtained from schist in the Brilonwald, in Sauerland. This acid was mistaken by Knop (*Annalen*, 1844, 49, 122) for usnic acid.

Umbilicaric acid, lecanoric acid, and a substance which may be gyrophoric acid were obtained from *Gyrophora polyrrhiza*.

Contrary to Hesse's statement (Abstr., 1903, i, 706), *Lepraria latebrarum* contains neither usnic nor talebraric acids. The appearance of hydroxyroccellic acid (Hesse, *loc. cit.*) must have been due to oxidation of the roccellic acid during the recrystallisation from boiling glacial acetic acid.

Rhizoplaca opaca (*Lecanora chrysoleuca* β -*opaca*, *Parmelia rubina* β -*opaca*, *Squamaria chrysoleuca* β -*opaca*), gathered from gneiss blocks

near Sölden, in the Oetzthal, in Tyrol, contains usnic, placodiolic, and rhizoplacic acids.

Placodiolic acid, previously termed placodiolin (Abstr., 1898, i, 90), is soluble in aqueous sodium hydrogen carbonate, and is reprecipitated by hydrochloric acid.

Rhizoplacic acid, $C_{21}H_{40}O_5$, crystallises in white, tetragonal leaflets, melts at 94—95°, and is soluble in warm ether, hot alcohol, chloroform, benzene, glacial acetic acid, or aqueous alkali hydroxides or carbonates; the solution in aqueous potassium hydroxide forms a lather. In concentrated sulphuric acid, the acid dissolves to form a lemon-yellow solution which, on exposure to air, deposits the unchanged white substance.

Usnea microcarpa, from South Tyrol, contains 3.3 per cent. of *d*-usnic and 0.1 per cent. of usnaric acid. Salazinic acid, from *Parmelia conspersa*, has been converted by boiling acetic anhydride into salazinic acid melting at 206—207° (compare Hesse, *loc. cit.*).

Gasparrinia sympagea contains parietin.

Theloschistes flavicans contains parietin and a colourless substance, which crystallises in spherical aggregates of thin leaflets, melts at 240—245°, and is insoluble in aqueous alkali hydroxides or concentrated sulphuric acid.

Ochrolechia androgyna (*Lecanora subtartarea*) contains gyrophoric acid, calyciarin, and a small amount of a substance which crystallises in thick, colourless prisms.

l-Usnic acid, a substance which forms colourless, slender crystals and is insoluble in alcohol or chloroform, and a crystalline acid which is easily soluble in alcohol and moderately so in glacial acetic acid and aqueous sodium hydrogen carbonate, from which it is reprecipitated on addition of hydrochloric acid, were isolated from *Cladonia incrassata*, obtained from Wildenloh in Oldenburg. The occurrence of ramalic acid (Hesse, this vol., i, 138), which may be identical with protocetraric acid, in *Ramalina farinacea* is confirmed. The purplish-violet coloration shown by *Physcia endococcina* when treated with potassium hydroxide is due to the presence of the two anthracene colouring matters, rhodophycin, which is red, crystallises in small leaflets, and decomposes above 260°, and endococcin, which crystallises in yellow prisms. The lichen contains also atranoric acid and zeorin. G. Y.

***m*-Halogen-benzaldehydes.** CARL METTLER (*Ber.*, 1905, 38, 2809—2812).—*m*-Halogen-benzaldehydes are prepared by electrolytic reduction of the corresponding halogen-benzoic acids to the halogen-benzyl alcohols (this vol., i, 436), and oxidation of these with nitric acid in sulphuric acid solution at 40—50°.

m-Bromobenzaldehyde prepared by this method boils at 228—230° under 726 mm. pressure (compare Baeyer and Wirth, Abstr., 1895, i, 288). A specimen prepared by Einhorn and Gernsheim's method (Abstr., 1895, i, 281) boiled at 224—226° under 726 mm. pressure. The phenylhydrazone melts at 143—144°; the oxime melts at 73°.

β -Hydroxy- β -5-chloro-2-nitrophenylethyl methyl ketone melting at 106° is prepared by the condensation of 5-chloro-2-nitrobenzaldehyde with acetone in presence of trisodium phosphate. G. Y.

Thiele's Xylene-oxidation and Terephthalaldehyde-green.

PAUL CLAUSSNER (*Ber.*, 1905, **38**, 2860—2862).—The oxidation of *p*-xylene by means of a mixture of acetic anhydride and sulphuric acid (Thiele and Winter, *Abstr.*, 1900, i, 500) leads to the formation of terephthalaldehyde tetra-acetate and *p*-tolualdehyde diacetate; the former is the principal product if the reaction is carried out at 10—18°, the latter, if at -2° to -10°. *p*-Tolualdehyde diacetate, $C_7H_7 \cdot CH(OAc)_2$, is formed also by the action of acetic anhydride on *p*-tolualdehyde at 150—180°; it crystallises in colourless, glistening leaflets, melts at 69°, is soluble in cold alcohol, but insoluble in aqueous alkali hydroxides, and forms a leuco-malachite-green when heated with dimethylaniline and zinc chloride.

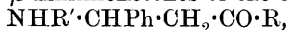
Octamethyltetraminotetraphenyl-*p*-xylene, $C_6H_4[CH(C_6H_4 \cdot NMe_2)_2]_2$, is formed by the condensation of terephthalaldehyde tetra-acetate and dimethylaniline in presence of zinc chloride; it forms a crystalline powder, melts and decomposes at 243—248°, is easily soluble in benzene or dilute acetic acid, but is insoluble in water, alcohol, or ether, and, on oxidation with lead peroxide in acetic acid solution, yields terephthalaldehyde-green, which closely resembles malachite-green. G. Y.

Decomposition of the Sodium Derivative of *iso*Nitrosoacetophenone.

C. H. SLUITER (*Rec. Trav. chim.*, 1905, [ii], **24**, 365—367).—The sodium derivative of *isonitrosoacetophenone* is coloured, and on heating in aqueous solution is decomposed according to the equation $COPh \cdot CH : NONa = Ph \cdot CO_2Na + HCN$; a determination of the velocity of this reaction, using a colorimetric process, shows it to be unimolecular; the velocity-coefficient, which is independent of the concentration for values between 1 and 5 per cent., increases with the temperature, and diminishes on the addition of a small quantity ($\frac{1}{2}$ mol.) of sodium hydroxide, becoming normal again as the quantity is increased to 10 mols. In alcoholic solution, the velocity-coefficient is also diminished, the diminution being less in the case of methyl than of ethyl alcohol. M. A. W.

Properties of β -Anilinoketones derived from Fatty Ketones.

CHARLES MAYER (*Bull. Soc. chim.*, 1905, [iii], **33**, 958—961. Compare this vol., i, 214, 357).— β -Anilinoketones of the constitution



where R is an alkyl, R' a phenyl or substituted phenyl group, are decomposed by the action of concentrated acids, acid chlorides, phenylcarbimide, or of piperidine, forming the unsaturated ketone,



and the corresponding aniline, anilide, or phenylcarbamide. On the other hand, the action of phenylhydrazine or semicarbazide hydrochloride, or of ethyl acetoacetate in presence of piperidine, leads to the decomposition of the β -anilinoketone into its generators: the fatty ketone, the aniline, and benzaldehyde, which is obtained as the phenylhydrazone or semicarbazone, or as ethyl benzyldenebisacetoacetate.

G. Y.

Addition of Acids and Salts to $\alpha\beta$ -Unsaturated Ketones. DANIEL VORLÄNDER (*Annalen*, 1905, 341, 1—80. Compare Abstr., 1903, i, 495, 632; 1904, i, 65).—The author's theory as to the formation of additive products of acids, salts, or the halogens with unsaturated ketones is discussed in the light of earlier experiments (*loc. cit.*) and of his later work. Two series of additive products are formed; the coloured unstable additive products, type A, have a very great velocity of formation, whilst that of the colourless, stable products, type B, is easily measurable.

[With C. SIEBERT.]—Molecular proportions of aldehydes and acids readily combine, as has been previously observed, the additive product belonging to type A but being only faintly coloured. At lower temperatures, these derivatives of aromatic aldehydes combine with a second molecule of halogen acid. The constitution of these additive products is regarded as analogous with that of the cyanohydrins. Hydrogen bromide and benzaldehyde yield at the ordinary temperature benzylidene bromide, but hydrogen chloride does not give the corresponding chloride.

Benzaldehyde monohydrobromide, $\text{CHBrPh}\cdot\text{OH}$, is formed at -19° as colourless crystals or leaflets, loses hydrogen bromide rapidly on exposure to the air, and is decomposed by water. *Anisaldehyde monohydrochloride*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}\cdot\text{HCl}$, formed at the ordinary temperature, crystallises in needles; at from -15° to -75° , the *dihydrochloride* is produced and forms a grey mass. The *monohydrobromide* is formed in acetic acid or petroleum solution, and crystallises in colourless needles. *Piperonal monohydrochloride*, $\text{C}_8\text{H}_6\text{O}_3\cdot\text{HCl}$, is obtained from -15° to the ordinary temperature; the *dihydrochloride* is formed at -75° ; both are yellow; the *monohydrobromide* forms yellow, prismatic crystals. No definite substance is formed from vanillin.

Chloral monohydrochloride, $\text{CCl}_3\cdot\text{CHO}\cdot\text{HCl}$, is a white, crystalline mass, and at -75° takes up no more hydrogen chloride. The polymerides, meta- and para-chloral, do not combine with hydrogen chloride. *Chloral monohydrobromide*, $\text{CCl}_3\cdot\text{CHO}\cdot\text{HBr}$, is a white, crystalline powder. *Bromal monohydrobromide* was obtained.

The temperature interval in which the additive products of the ketones are formed is lower and more limited than that of the other carbonyl derivatives. Many mono- and di-ketones react at the ordinary temperature with the hydrogen haloids, but not at 0° . The following substances form additive products at -75° : benzophenone, acetophenone, deoxybenzoin, benzil, anthraquinone, and phenanthraquinone; benzil does not form an additive product above -18° , and benzophenone not at -12° , but at -17° . Benzoin, anthraquinone, alizarin, and phenanthraquinone do not form compounds above -18° ; benzylacetone and benzylacetophenone react from -15° to -18° , and form several additive products according to the length of the treatment with the acid.

Phenolethylene derivatives form intensely coloured additive products of type A. It follows, therefore, that the carbonyl oxygen of unsaturated ketones is not essential for the development of colour. The colour would rather appear to be dependent on an interaction of the acid with the ethylene linking, and possibly the aromatic nucleus.

Anethole, isosafrole, isoapiole, isomethyleugenole, and asarone give such coloured additive products, but they cannot be isolated. A liquid compound is obtained from benzene at -75° , which contains three mols. (?) of hydrogen chloride. Unsaturated hydrocarbons do not yield additive products. Anisylideneacetophenone yields a *dipicrate*, $C_{16}H_{14}O_2 \cdot 2C_6H_3O_7N_3$, which crystallises in orange-coloured needles melting at about 87° . *Piperonalacetophenone dipicrate*,

$C_{16}H_{12}O_3 \cdot 2C_6H_3O_7N_3$, crystallises in orange needles melting at $126-128^{\circ}$. *Cinnamylideneacetophenone dipicrate*, $C_{17}H_{14}O_2 \cdot 2C_6H_3O_7N_3$, crystallises in yellow needles melting at $115-117^{\circ}$. *Benzylideneacetophenone dipicrate*, $C_{15}H_{12}O_2 \cdot 2C_6H_3O_7N_3$, crystallises in pale yellow needles melting at $93-97^{\circ}$. *Anisylidenepinacolin dipicrate*, $C_{14}H_{18}O_2 \cdot 2C_6H_3O_7N_3$, crystallises in yellow needles melting at $157-159^{\circ}$. *Dipiperonylideneacetone monopicrate* crystallises in red needles melting at $151-153^{\circ}$. *Anisylidene* and *piperonylidene*pinacolin were prepared in the same manner as benzylidenepinacolin; the former melts at 34° after distillation under reduced pressure, and the latter crystallises from petroleum in needles melting at 96° .

[With O. ROLLE.]—Anisylideneacetophenone forms a *dihydrochloride*, type A, $C_{16}H_{14}O_2 \cdot 2HCl$, crystallising in dark red needles or flattened prisms; when kept in petroleum saturated with hydrogen chloride, it is transformed into the *monohydrochloride*, type B, crystallising in colourless plates or leaflets, melting and decomposing at $86-88^{\circ}$ and easily decomposed by water. The following substances yield additive products with hydrogen chloride, which were not isolated in a pure state: piperonylideneacetophenone, dipiperonylideneacetone, methyl *p*-methoxycinnamate, and *p*-hydroxybenzylideneacetophenone; similar compounds with hydrogen bromide were obtained from anisylideneacetophenone, *p*-hydroxybenzylideneacetophenone, and methyl *p*-methoxycinnamate.

The *hydrochloride*, type B, of benzylideneacetophenone condenses with benzaldehyde when the mixture is saturated with hydrogen chloride, forming a compound, $COPh \cdot CH(CHPhCl)_2$; it crystallises in white needles from methyl alcohol and melts at 155° .

[With C. SIEBERT.]—The additive products formed by the action of bromine on solutions of aromatic ketones belong to type B. The coloured additive products of type A are apparently formed under certain conditions, as by the action of bromine vapour on solid dry dibenzylideneacetone. When dibenzylideneacetone is brominated, substances are formed containing bromine, besides the known tetrabromide. Dicinnamylideneacetone forms an *octobromide*, $C_{21}H_{18}OBr_8$, which crystallises in needles melting and decomposing at $200-202^{\circ}$.

Diphenyldimethyltetrahydropyrone and the so-called dibenzylidenediethyl ketone, $C_{19}H_{18}O$ (shown by Japp and Maitland, *Trans.*, 1904, 85, 1473, to be dimethylcyclopentanone), show an abnormal behaviour towards sulphuric acid, in that the former, which does not possess an ethylene linking, gives a yellow coloration with sulphuric acid, whilst the latter, which as an unsaturated ketone does possess an ethylene linking, yields no such coloration. Dimethylcyclopentanone yields, on oxidation with chromic and sulphuric acids, an *acid*, $C_{17}H_{14}O_3$,

of unknown constitution, which crystallises in colourless needles melting at 175° . The *silver* salt, $C_{17}H_{13}O_5Ag$, was prepared. The *ethyl* ester, $C_{17}H_{13}O_2OEt$, melts at $118-120^{\circ}$, and the *methyl* ester at 73° .

Addition of Ethyl Sodiomalonate to the Sodium Salts of Unsaturated Acids.—The mechanism of the reaction is discussed at considerable length. Ethyl sodiomalonate shows a greater tendency to form additive products with the esters of α -unsaturated acids than with the sodium salts. Thus the sodium salts of crotonic, sorbic, cinnamyl-acrylic, cinnamic, phenyl- $\beta\gamma$ -crotonic, and benzylidenemalononic acids do not combine with ethyl sodiomalonate, whilst their esters react easily. On the other hand, since the sodium salts of the β - and δ -benzylidenelævulic acid and of cinnamoylanthranilic acid react, it would appear that the saline properties do not prevent the addition. The esters of the hydroresorcinols and the sodium salts of the diketones do not react with the sodiomalonate; a similar inactivity is observed in the case of the sodium salts of *p*-hydroxybenzylideneacetophenone and the ester of *p*-coumaric acid. The disodium salt and the salt of the mono-ethyl ester of malonic acid do not react in the same way with the unsaturated ketones and esters as does the di-ethyl ester. The presence of acids prevents the interaction both of ethyl malonate and of malonic acid with cinnamic acid.

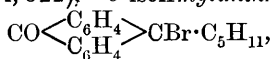
Ethyl malonate does not interact either with unsaturated esters or ketones possessing one carbonyl group. Since ethyl sodiomalonate in alcoholic solution reacts with such substances, it would appear that the presence of sodium ethoxide favours the addition by the formation of additive products. In certain cases, these intermediate additive products can be isolated, but it is found that they are less reactive than the unsaturated ester itself. The formation of such products is entirely prevented when the reaction of the unsaturated ester and the ethyl sodiomalonate is carried out in the presence of ethyl malonate as solvent. It would seem from these experiments that a direct addition of the sodiomalonate to the unsaturated ester is the starting-point of the greater number of these reactions.

[With PAUL WEISSHEIMER.]—The additive products which are formed from ethyl sodiomalonate and dimethylpyrone belong to type A, since they are decomposed by solvents and show the reactions of the components. The molecular additive *product*, $C_{14}H_{19}O_6Na$, is formed in benzene or ethereal solution, and crystallises in slender, colourless needles. The *compound*, $C_{15}H_{21}O_6Na$, of dimethylpyrone and ethyl sodiomethylmalonate crystallises in hexagonal leaflets or prisms. The *compound*, $C_{12}H_{15}O_6Na$, of dimethylpyrone and methyl sodiomalonate crystallises from benzene in needles.

Amines form two classes of additive products. The compounds of tertiary amines with alkyl haloids belong to type B, whereas the acid compounds of amines are classed under type A. Observation would show that two distinct processes occur in the addition of acids to amines, differing in the energy transformations which accompany the reaction. The observations of earlier investigators are discussed, and the influence of water and other solvents on the formation of these additive compounds is considered from this point of view.

In the addition of two salts, a far more complicated process is observed than in the case of amines. It is thought that double salts are additive compounds of the type A, whilst complex salts belong to type B. K. J. P. O.

Reactions of isoAmylanthrone Chloride and Bromide. E. JUNGERMANN (*Ber.*, 1905, **38**, 2868—2873. Compare Liebermann and Lindenbaum, this vol., i, 522).—9-isoAmylanthrone bromide,



is formed by the action of hydrogen bromide on isoamyloxanthranol in benzene solution; it crystallises in white rhombohedra and melts at

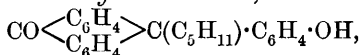
97—98°. 9-Ethoxy-9-isoamyl-10-anthrone, $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}(\text{C}_5\text{H}_{11}) \cdot \text{OEt}$,

prepared by boiling isoamylanthrone chloride in ethyl alcohol in a reflux apparatus, crystallises in colourless prisms, melts at 53°, deliquesces in contact with organic solvents, and when treated with hot concentrated sulphuric acid forms a red coloration and the intramolecular condensation product, $\text{C}_{19}\text{H}_{14}\text{O}$, melting at 206° (Liebermann and Landshoff, *Abstr.*, 1882, 608). 9-Methoxy-9-isoamyl-10-anthrone, $\text{C}_{20}\text{H}_{22}\text{O}_2$, forms colourless crystals and melts at 67—69°. 9:10-Diphenoxy-9:10-isoamylene-

dihydroanthracene, $\text{OPh} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_5\text{H}_{10} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{OPh}$, formed when isoamylan-

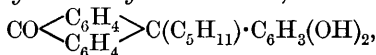
throne chloride is boiled with phenol (2 mols.) in benzene solution in a reflux apparatus, crystallises in yellow needles, melts at 67—71°, is easily soluble in all organic solvents, but is insoluble in aqueous alkali hydroxides, does not form an acetyl derivative, and when treated with hot concentrated sulphuric acid yields the intramolecular condensation product, $\text{C}_{19}\text{H}_{14}\text{O}$.

9-Hydroxyphenyl-9-isoamyl-10-anthrone,



is formed by the action of phenol (1 mol.) on isoamylanthrone chloride in cold glacial acetic acid solution; it crystallises in colourless prisms, melts at 228°, and is moderately soluble in dilute potassium hydroxide. The acetyl derivative, $\text{C}_{25}\text{H}_{23}\text{O}_2\text{Ac}$, crystallises in colourless needles and melts at 148—150°.

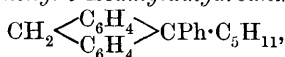
9-Dihydroxyphenyl-9-isoamyl-10-anthrone,



formed from resorcinol and isoamylanthrone chloride, crystallises in colourless prisms, melts at 262°, and is easily soluble in dilute potassium hydroxide. The diacetyl derivative, $\text{C}_{29}\text{H}_{28}\text{O}_5$, crystallises in colourless needles and melts at 161°.

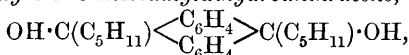
9-Phenyl-9-isoamyl-10-anthrone, $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CPh} \cdot \text{C}_5\text{H}_{11}$, is formed by the action of aluminium chloride on isoamylanthrone chloride in benzene solution; it crystallises in colourless prisms and melts at 139°. When heated with hydriodic acid and red phosphorus in a reflux

apparatus, it forms 9-phenyl-9-isoamylidihydroanthracene,



which separates from alcohol in colourless crystals, melts at 85° , is easily soluble in all organic solvents, and when treated with bromine in carbon disulphide solution yields 10-bromo-9-phenyl-9-isoamylidihydroanthracene, $\text{CHBr} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{CPh} \cdot \text{C}_5\text{H}_{11}$. This separates from light petroleum in colourless crystals and melts at $134\text{--}137^\circ$.

9:10-Dihydroxy-9:10-diisoamylidihydroanthracene,



formed by the action of magnesium isoamyl bromide on isoamyloxanthranol in ethereal solution, separates on evaporation of its ethereal solution in colourless crystals, melts at $170\text{--}174^\circ$, dissolves easily in benzene, more sparingly in alcohol or light petroleum, to form solutions with blue fluorescence, and gives a red coloration with hot concentrated sulphuric acid. On addition of concentrated sulphuric acid to its solution in glacial acetic acid, it yields 9:10-diamylenedihydroanthracene,

$\text{C}_5\text{H}_{10} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \cdot \text{C}_5\text{H}_{10}$, which crystallises in yellow prisms, melts at $103\text{--}108^\circ$, dissolves in all organic solvents to form solutions with blue fluorescence, and decolorises bromine (2 mols.) in carbon disulphide solution with evolution of hydrogen bromide. When boiled for 5—10 minutes with hydriodic acid of sp. gr. 1.96, it is reduced to

9:10-diisoamylanthracene, $\text{C}_5\text{H}_{11} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \cdot \text{C}_5\text{H}_{11}$, which crystal-

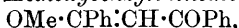
lises in yellowish-green needles, melts at $132\text{--}137^\circ$, is easily soluble in organic solvents, and is not reduced when boiled with hydriodic acid and red phosphorus for three hours. G. Y.

Wislicenus's Supposed Isomeride of Dibenzoylmethane.

C. H. SLUITER (*Rec. Trav. chim.*, 1905, [ii], 24, 368—371).—Independently of Ruhemann and Watson (*Trans.*, 1904, 85, 456), the author has proved that the compound described by Wislicenus as an isomeride of dibenzoylmethane (*Abstr.*, 1900, i, 37) is α -ethoxybenzylideneacetophenone, $\text{OEt} \cdot \text{CPh} \cdot \text{CH} \cdot \text{COPh}$. The compound appears to exist in

two stereoisomeric forms, $\begin{array}{c} \text{COPh} \cdot \text{C} \cdot \text{H} \\ | \\ \text{OEt} \cdot \text{C} \cdot \text{Ph} \end{array}$ and $\begin{array}{c} \text{COPh} \cdot \text{C} \cdot \text{H} \\ | \\ \text{Ph} \cdot \text{C} \cdot \text{OEt} \end{array}$, for when

first prepared it melts at 61° ; the melting point slowly changes until after some months it becomes constant at 77° . An attempt to prepare α -ethoxybenzylideneacetophenone by the action of ethyl iodide on the sodium derivative of dibenzoylmethane resulted in the formation of $\alpha\alpha$ -dibenzoylpropane, $\text{CHEt}(\text{COPh})_2$ (compare Auger, *Ann. Chim. Phys.*, 1891, [vi], 22, 348). α -Methoxybenzylideneacetophenone,



prepared by the action of sodium methoxide on bromobenzylideneacetophenone, is a yellow oil boiling at $220\text{--}222^\circ$ under 16 mm. pressure, and solidifying in a mixture of solid carbon dioxide and alcohol to crystals which melt at -11° . M. A. W.

Action of Mercaptides on Quinones. JOHN L. SAMMIS (*J. Amer. Chem. Soc.*, 1905, 27, 1120—1127).—An improved method is described for the preparation of tetraethylthiolquinone, first obtained by Grindley and Sammis (Abstr., 1897, i, 403), by means of which a yield amounting to 95 per cent. of the theoretical can be obtained.

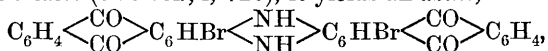
When an alcoholic solution of lead acetate is added to a solution of tetraethylthiolquinol, a compound, $C_6(SET)_4(OPb \cdot OAc)_2$, is obtained as a yellow, crystalline precipitate; the formation of this lead salt serves as a delicate test for tetraethylthiolquinol.

The substance described as tetraethylthiolquinonedibenzoyldithiobenzoylacetal (*loc. cit.*) is now found to be tetraethylthiolquinol dibenzoate, $C_6(SET)_4(OBz)_2$.

When a solution of sodium ethoxide is added to tetraethylthiolquinone moistened with a little alcohol, diethylthioldiethoxyquinol dibenzoate, $C_6(SET)_2(OEt)_2(OBz)_2$, is obtained, which crystallises in equilateral, six-sided plates, melts at 184—184.5°, and is soluble in benzene, chloroform, or ether.

The results of this investigation have shown that the action of mercaptides on quinones is a process of substitution and reduction, no additive products having yet been isolated. E. G.

[1:4-Dibromo-2-aminoanthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158474).—Bromination of β -aminoanthraquinone in aqueous suspension or in indifferent solvents with a slight excess of bromine yields 1:4-dibromo-2-aminoanthraquinone, which crystallises in orange needles, melts at 239—240°, and dissolves in acetic acid, nitrobenzene, pyridine, hot alcohol, or concentrated sulphuric acid to yellow solutions. When heated with sodium acetate and metallic salts (this vol., i, 720), it yields an azine,



dissolving in hot nitrobenzene or aniline to a greenish-blue solution. Water precipitates the azine in blue flocks from its olive-brown solution in concentrated sulphuric acid. A fast greenish-blue dye is obtained on reducing it in alkaline solution. C. H. D.

Aryl Ethers of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 158531).—The aryl ethers of anthraquinone derivatives may be prepared by heating halogen, nitro-, or sulpho-derivatives of anthraquinone with alkali phenoxides, the negative group being replaced by the phenol residue.

Erythroxyanthraquinone phenyl ether (1-phenoxyanthraquinone), prepared by heating 1-bromo- or 1-nitro-anthraquinone or potassium anthraquinone-1-sulphonate with potassium phenoxide at 170°, crystallises from ethyl acetate in radiating groups of yellow prisms and melts at 145°. 1:5-Diphenoxyanthraquinone separates from acetic acid or nitrobenzene in long, yellow needles and melts at 215°.

1:5-Di- β -naphthoxyanthraquinone, from 1:5-dinitroanthraquinone and potassium β -naphthoxide, crystallises from acetic acid in bright yellow needles and melts at 243—245°. 1:5-Di-o-tolylxyanthraquinone forms golden leaflets and melts at 190°; the p-tolyl ether forms long,

yellow needles and melts at 223—225°. *2-Phenoxyanthraquinone* melts at 153°, *chrysazin diphenyl ether* melts at 189—190°.

It is also possible to replace one of several negative groups present in the molecule. Thus 1-nitroanthraquinone-6-sulphonic acid and potassium phenoxide yield 1-*phenoxyanthraquinone-6-sulphonic acid*, the ammonium salt of which forms glistening, yellow leaflets. 1-Anilino-5-*phenoxyanthraquinone*, from 5-nitro-1-anilinoanthraquinone, forms red, glistening needles and melts at 188—190°.

The preparation of other similar derivatives is described.

C. H. D.

Stereoisomeric Menthols. IWAN KONDAKOFF (*J. pr. Chem.*, 1905, [ii], 72, 185—193).—It has been held by various authors that *d*-menthol forms an intermediate stage in the conversion of *l*-menthol into *tert*-menthol or its derivatives. Contrary to this view is the formation of Δ^3 - and not Δ^2 -menthene from *l*-menthol, and the fact that *d*-menthol is more stable than is generally assumed.

The ethereal oil of *Bucco* leaves (Abstr., 1897, i, 227) is now found to contain (1) dipentene and limonene, (2) a ketone which boils at 86° under 10 mm. pressure and has $[\alpha]_D - 51^\circ$, and (3) a mixture of diosphenol with a compound of diosphenol and an acid melting at 94°. The ketone, which is more easily obtained from *Barosma serratifolia*, forms a glistening, crystalline *hydrazone* melting at 80° and two *semicarbazones*, of which the one only slightly soluble in alcohol melts at 180°, whilst the other, more soluble, melts at 123°. On treatment of the former semicarbazone with sulphuric acid there is obtained an inverted ketone, which boils at 85.5—86° under 10 mm. pressure, has a sp. gr. 0.897 at 19.5°, $[\alpha]_D - 22.3^\circ$, $n_D 1.45169$, and on reduction with sodium in methyl-alcoholic solution yields *d*-menthol. This yields *d*-menthene and forms haloid esters consisting of a mixture of unstable derivatives of *tert*-menthol and stable dextrorotatory derivatives of *d*-menthol.

On reduction by Leuckart's method, *d*-menthone yields *d*-formylmenthylamine, melting at 117—118° and having $[\alpha]_D + 154.47^\circ$, together with a small amount of the *l*-amine. *d*-isoMenthol, obtained from *d*-menthylamine or together with *d*-menthol on reduction of *l*- or *d*-menthone, boils at 83.5—84°, has $[\alpha]_D + 25.64^\circ$, and on oxidation yields *d*-menthone. The corresponding *l*-isomenthol is unknown.

Brünel's *i*-menthol (this vol., i, 197), melting at 29—31°, is probably identical with Richtmann and Kremer's substance (Abstr., 1897, i, 84). A second *i*-menthol is described by Beckmann (Abstr., 1897, i, 248).

The properties of the *i*-menthol described by Baehr (*Synthese eines inactiven menthens*, Leipzig, 1898) resemble those of *tert*-menthol, but it may be a new secondary *i*-menthol if Hagemann's acid is a δ -keto-, and not a β -keto- or mixture of β - and δ -keto-acids (Merling, this vol., i, 349). *tert*-Menthol is optically inactive, does not form a urethane, and when treated with carbanil loses water, forming a menthene which boils at 170—175° and has a sp. gr. 0.812 at 20°/4° and $n_D 1.45627$. *tert*-Menthol forms a liquid, but not a solid, *nitrosochloride*. This boils at 128—152° under 11 mm. pressure, or, after

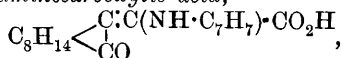
treatment with hydrogen chloride in ethereal solution, at 128—140°, distils in a current of steam without appreciable decomposition, and loses hydrogen chloride when treated with sodium ethoxide, acetates in acetic acid solution, or alcoholic potassium hydroxide, forming nitroso-menthene.

Reduction of diosphenol leads to the formation of a liquid *i*-menthol, which boils at 98—100·5° under 12 mm. or at 214·5—216° under 759 mm. pressure, has a sp. gr. 0·9052 at 20° and n_D 1·464456, and may be identical with Brünel's α -thymomenthol (*loc. cit.*). It forms an inactive iodide which yields an *i*-menthene boiling at 168—169°, and having a sp. gr. 0·8264 at 19·8°/4°. G. Y.

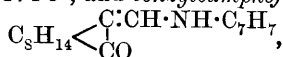
Condensation Compounds of Camphoroxalic Acid and Amines. J. BISHOP TINGLE and WILLIAM E. HOFFMAN, jun. (*Amer. Chem. J.*, 1905, **34**, 217—254. Compare *Trans.*, 1890, **57**, 652; *Abstr.*, 1897, i, 484; 1898, i, 443; 1899, i, 444; 1900, i, 302; 1901, i, 632).—*Copper, silver, barium, calcium, and ferric camphoroxalates* are described.

The action of amines on camphoroxalic acid has been studied. With β -naphthylamine, β -naphthylamine β -naphthylcamphorformeneamine-carboxylate is produced, which melts at 169°; the corresponding acid has been described previously (*Abstr.*, 1900, i, 302). When either the acid or the naphthylamine salt is heated above its melting point, β -naphthylcamphorformeneamine, $C_8H_{14} \begin{smallmatrix} \text{C}:\text{CH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7 \\ | \\ \text{CO} \end{smallmatrix}$, is obtained, which crystallises in slender, pale yellow prisms and melts at 173°. α -Naphthylamine α -naphthylcamphorformeneamine-carboxylate melts at 165°.

With *p*-toluidine, the following compounds were obtained. *p*-Tolylcamphorformeneaminecarboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{C}:\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}_2\text{H} \\ | \\ \text{CO} \end{smallmatrix}$, crystallises from benzene in pale yellow prisms and melts at 168°; the *p*-toluidine salt melts at 152°. *p*-Tolylcamphorformeneamine, $C_8H_{14} \begin{smallmatrix} \text{C}:\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me} \\ | \\ \text{CO} \end{smallmatrix}$, crystallises from alcohol in slender, yellow prisms and melts at 178°. *m*-Toluidine furnishes *m*-tolylcamphorformeneaminecarboxylic acid, $C_8H_{14} \begin{smallmatrix} \text{C}:\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}_2\text{H} \\ | \\ \text{CO} \end{smallmatrix}$, which crystallises from benzene in colourless needles and melts at 154°, and its *m*-toluidine salt melting at 126°; when these compounds are heated above the melting point, a viscous mass is produced in each case from which no definite compound can be isolated. Benzylamine yields benzylcamphorformeneaminecarboxylic acid,

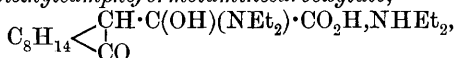


which crystallises in colourless prisms and melts at 140°, the benzylamine salt melting at 174·5°, and benzylcamphorformeneamine,

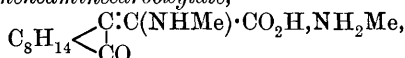


which crystallises in colourless prisms and melts at 96·5°.

Diethylamine reacts with camphoroxalic acid with formation of *diethylamine diethylcamphoformolaminecarboxylate*,



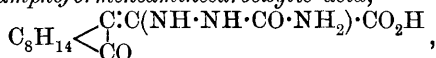
which crystallises from alcohol in colourless needles, melts at 139.5° , and when heated above its melting point is converted into a *compound*, $\text{C}_{15}\text{H}_{25}\text{ON}$, which crystallises in colourless needles and melts at 153° . Dimethylamine similarly yields *dimethylamine dimethylcamphoformolaminecarboxylate*, which crystallises in colourless needles, melts at 137.5° , and when heated above its melting point is decomposed with formation of a *compound*, $\text{C}_{13}\text{H}_{21}\text{ON}$, melting at 63° . *Methylamine methylcamphoformeneaminecarboxylate*,



melts at 172° , and when heated above this temperature is converted into *methylcamphoformeneamine*, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{NHMe} \\ | \\ \text{CO} \end{array}$, which crystallises in colourless needles and melts at 131° .

Benzamidine reacts with camphoroxalic acid to form a colourless, crystalline compound, $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_2$, which melts at 184° and becomes charred at a slightly higher temperature. Benzidine yields a greenish-yellow, crystalline *compound* which melts at 190° . When an alcoholic solution of camphoroxalic acid is heated with 4-nitro-*o*-toluidine under pressure at 150° for several hours, *o*-nitrotolylcamphoformeneamine, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2 \\ | \\ \text{CO} \end{array}$, is produced, which crystallises in bright yellow needles and melts at 192° .

Semicarbazide reacts with camphoroxalic acid with formation of *semicarbazidocamphoformeneaminecarboxylic acid*,



which crystallises from alcohol in stout, colourless prisms, melting at 200° , and from boiling glacial acetic acid in groups of slender needles, melting at $209-210^\circ$; the relationship between these two forms is being investigated.

By the action of benzenesulphonic chloride on phenylcamphoformeneamine, the *phenylsulphone*, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{NPh} \cdot \text{SO}_2\text{Ph} \\ | \\ \text{CO} \end{array}$, is produced, which crystallises in colourless needles and melts at 133° . Acetyl chloride reacts with *p*-tolylcamphoformeneamine with formation of the *acetyl* derivative, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CH} \cdot \text{NAc} \cdot \text{C}_6\text{H}_4\text{Me} \\ | \\ \text{CO} \end{array}$, which is a colourless, crystalline compound melting at 161° . When β -naphthylcamphoformeneamine is treated with chloroacetyl chloride, a colourless, crystalline substance is obtained which melts at 63° and is very unstable. E. G.

New Terpene Alcohol in Myrtle Oil. HUGO VON SODEN and FRITZ ELZE (*Chem. Zeit.*, 1905, 29, 1031).—On subjecting the residues of high boiling point from Spanish myrtle oil to fractional distillation

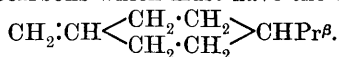
in a vacuum, the authors obtained a large fraction having a sp. gr. 0.975 at 15° and $\alpha_D + 28^\circ$ in a 100 mm. tube, which consisted, to the extent of about 80 per cent., of an ester $\text{CH}_3 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{17}$. This fraction, on hydrolysis with alcoholic potash, yielded an alcohol *myrtenol*, which was purified by conversion into *myrtenyl phthalate*, which separates from light petroleum (b. p. 100—125°) in hard, white crystals melting at 116°; the latter, on hydrolysis, yields pure *myrtenol*, which is a thick, colourless oil of a peculiar odour resembling myrtles; it boils at 220—221° under 751 mm. or at 79.5—80° under 3.5 mm. pressure, has a sp. gr. 0.985 at 15° and $\alpha_D + 49.25'$ in a 100 mm. tube. *Myrtenol* appears to be a cyclic primary alcohol containing a single double linking. P. H.

Constitution of the Group, N_2O_2 , of Pernitroso-compounds derived from Oximes. OTTORINO ANGELUCCI (*Annalen*, 1905, 341, 172—182).—The constitution of the group, N_2O_2 , of the pernitroso-compounds is best represented by the expression $\text{R}:\text{N} \cdot \text{O} \cdot \text{N}:\text{O}$. The peculiar behaviour of the pernitroso-compounds from camphoroxime and certain other oximes is due to the nature of the group combined with the nitroso-group, and not to the nitroso-group itself. Scholl's nitroimines (this vol., i, 181) are considered to be nitroso-compounds.

When pernitrosocamphor is reduced with aluminium amalgam, a mixture of the two stereoisomeric bornylamines is formed. If nitrosyl chloride (1 mol.) and camphoroxime (2 mols.) react in chloroform solution, molecular proportions of pernitrosocamphor and the hydrochloride of camphoroxime are formed. Nitrosyl chloride and sodium camphoroxime react quantitatively to form pernitrosocamphor.

K. J. P. O.

Synthetical and Natural Phellandrene. IWAN KONDAKOFF and IWAN SCHINDELMEISER (*J. pr. Chem.*, 1905, [ii], 72, 193—196. Compare Abstr., 1903, i, 845).—*tert.*-Carvomenthyl chloride, obtained from *tert.*-carvomenthol, boils at 83.5—84.5° under 12 mm. pressure, has a sp. gr. 0.932 at 20°/4°, and forms *tert.*-carvomenthene, which boils at 174—176°, has a sp. gr. 0.811 at 20°/4°, and $n_D 1.45709$. On treatment with bromine in strongly cooled light petroleum solution, this yields carvomenthene dibromide, which boils between 130° and 144° under 11 mm. pressure, has a sp. gr. 1.208 at 20°/4°, is optically inactive, and by alcoholic potassium hydroxide is converted into a hydrocarbon or mixture of hydrocarbons which must have the constitution



This distils in two fractions: the larger boils at 175—180°, has a sp. gr. 0.825 at 20°/4°, and $n_D 1.46693$; the smaller boils at 180—185°, has a sp. gr. 0.828 at 20°/4°, and $n_D 1.4673$. The hydrocarbon is not identical therefore with natural phellandrene. Both fractions are optically inactive and give a red coloration with sulphuric acid in acetic acid solution. A specimen of phellandrene from *Phellandrum aquaticum*, which boils at 165—168°, has a sp. gr. 0.844 at 20°/4°, $n_D 1.47575$, and $[\alpha]_D + 8.37'$ at 20°, reacts with hydrochloric acid in acetic acid solution to form a dextrorotatory chloro-derivative, $\text{C}_{10}\text{H}_{17}\text{Cl}$,

which melts at 110° and boils at 86° under 11 mm. pressure, and a dichloride, $C_{10}H_{18}Cl_2$, which boils at 122.5 — 125° under 16 mm. pressure, and has a sp. gr. 1.006 at $20^{\circ}/4^{\circ}$ and n_D 1.48516 at 20° (compare Pesci, *Abstr.*, 1886, 1038).
G. Y.

Constitution of Terpinene. T. AMENOMIYA (*Ber.*, 1905, 38, 2730—2732. Compare this vol., i, 603).—When terpinene nitronitrosite, formed by the nitration of terpinene nitrosite, is reduced in alcoholic solution with zinc dust and the product then submitted to distillation in a current of steam, rhombic prisms of carvenoneoxime, melting at 91 — 92° , are obtained. When terpinene nitrosite itself is reduced in a similar manner, carvenone is formed in small amount.

The bearing of these results on the constitution of terpinene is discussed.
A. McK.

Oil derived from Leaves and Stems of the Sweet Orange (*Citrus Aurantium*). GUSTAVE LITTERER (*Bull. Soc. chim.*, 1905, [iii], 33, 1079—1081).—The oil is of a bright yellow colour, has a sp. gr. 0.8603 at 15° , n_D 1.472 at 20° , and α_D $+56.46'$ in a 100 mm. tube. The principal constituents of the oil are *d*-camphene, limonene, geraniol, *d*-linalool (?), and citral (4 per cent.). The alcohols are present partly in the free state and partly as esters.
T. A. H.

Oil derived from the Leaves and Stems of the Lemon Tree (*Citrus Limonum*). GUSTAVE LITTERER (*Bull. Soc. chim.*, 1905, [iii], 33, 1081—1083).—The oil is yellow in colour, and is of a pleasant odour, has a sp. gr. 0.8824 at 15° , n_D 1.4725 at 23° , and α_D $+21.08'$ in a 100 mm. tube. It contains the same constituents as the oil obtained from the leaves and stems of the sweet orange (see preceding abstract), but contains more citral (24 per cent.) and esters and less camphene. The "total alcohol" is practically the same for both oils.
T. A. H.

Essential Oil of Patchouli. Action of Sulphuric Acid on Oil of Patchouli. ANNE W. K. DE JONG (*Rec. Trav. chim.*, 1905, [ii], 24, 309—310, 311—312).—The physical constants of the essences obtained from three varieties of patchouli are as follows: that from flowering patchouli has a sp. gr. 0.922 at 25° , $[\alpha]_D$ $-16.10'$ at 25° , 10 c.c. dissolve in 100 c.c. alcohol, it begins to distil at 130° , and 50 per cent. distils between 250° and 270° . That from Singapore patchouli has a sp. gr. 0.949 at 25° , $[\alpha]_D$ $-51.24'$ at 25° , 10 c.c. dissolve in 60 c.c. alcohol, it begins to distil at 230° , 60 per cent. passing over between 250° and 270° . That from Java patchouli has a sp. gr. 0.929 at 25° , $[\alpha]_D$ $-42.18'$ at 25° , 10 c.c. dissolve in 7.5 c.c. of alcohol; it begins to distil at 145° , and 70 per cent. passes over between 250° and 270° .

By the action of concentrated sulphuric acid on essence of patchouli, a sesquiterpene, $C_{15}H_{24}$, boiling at 260 — 263° under 740 mm. pressure, is obtained; the hydrocarbon derived from Singapore patchouli has a sp. gr. 0.915 at 25° and $[\alpha]_D$ -1° , whilst that obtained from Java patchouli has a sp. gr. 0.897 at 25° and $[\alpha]_D$ $-1.5'$ at 25° . The author proposes the name *dilemene* (from *dilem*, the Malay name of the plant)

for this sesquiterpene, which is probably identical with the compound obtained by Soden and Rojahn by fractional distillation of patchouli oil (compare Abstr., 1904, i, 904). M. A. W.

Scammony Resins. P. GUIGUES (*J. Pharm. Chim.*, 1905, [vi], 22, 241—246).—Genuine scammony resin of pharmacy contains 20 per cent. of resin insoluble in ether, the rest being soluble; the insoluble resin has $\alpha_D - 20^\circ 43'$ and $n_D 1.3659$ at 15° ; the corresponding values for the soluble resin are $-21^\circ 43'$ and 1.3659 respectively. M. A. W.

The Nature of the Sugars of certain Glucosides. HENRI TER MEULEN (*Rec. Trav. chim.*, 1905, [ii], 24, 444—483).—It has been shown by Croft Hill that the hydrolysis of maltose by maltase is a reversible reaction (compare Trans., 1898, 73, 634; 1903, 83, 578), and by Tammann that the hydrolysis of amygdalin by emulsin is retarded by the addition of dextrose to the solution (compare Abstr., 1889, 566; 1892, 899). In the present paper, the author shows that the hydrolytic action of any enzyme on its specific glucoside is retarded by the addition to the solution of the sugar that forms one of the products of the reaction; and, further, the nature of the sugar formed by the hydrolysis of a glucoside can in this way be determined. The experiments were conducted as follows: equal volumes of the glucoside solution were taken and to each was added a definite quantity of a sugar (galactose, lævulose, sucrose, maltose, rhamninoase, or dextrose) and of the specific enzyme; after about two hours, the enzyme was destroyed and the extent to which the glucoside had suffered hydrolysis was measured by separating and weighing the product, other than sugar, of the reaction; thus, in the case of xanthorhamnin (compare Votoček and Frič, Abstr., 1901, i, 161; Tanret, Abstr., 1900, i, 78, 185), the glucoside was hydrolysed to the extent of 55—56 per cent. either in solution alone or in solutions containing dextrose, lævulose, galactose, rhamnose, sucrose, lactose, maltose, or raffinose, whilst in a solution containing rhamninoase, which is the sugar formed during the hydrolysis, only 39 per cent. of the glucoside was decomposed. Similar experiments conducted on salicin, amygdalin, æsculin, arbutin, coniferin, indican, saponin, and on certain glucosides which could not be obtained in a pure state, such as gluconasturtein, glucotropeolin, glucocochlearin, and gluconapin, showed that in each of these cases dextrose is the sugar formed by the hydrolysis of the glucoside.

The presence in solution of a specific sugar only retards the hydrolysis of the glucoside in the initial stages of the reaction; towards the end of the reaction, the hydrolysis is more complete in the liquid containing the sugar than in the liquid to which no sugar has been added; this is because the enzyme is less rapidly destroyed in a solution containing sugar than in an aqueous solution. M. A. W.

Gentiamarin. GEORGES TANRET (*Bull. Soc. chim.*, 1905, [iii], 33, 1071—1073. Compare this vol., i, 655).—The alcoholic extract of gentian root, from which gentiopierin separates (*loc. cit.*), contains in addition the amorphous glucoside *gentiamarin*, which may be obtained

by washing the extract with ether, dissolving the insoluble matter in water, and adding to this solution (1) a large excess of tannic acid and (2) a solution of magnesium sulphate in water. In this way a "tannate" of the glucoside is precipitated from which the latter may be regenerated by adding hydrated lead oxide to an alcoholic solution of the "tannate." Gentiamarin is bitter, miscible with water or alcohol, has $[\alpha]_D -80-90^\circ$, and the composition $C_{16}H_{22}O_{10}$ or $C_{16}H_{20}O_{10}$. On hydrolysis with acids, it yields dextrose and an amorphous, brown, insoluble substance. Emulsin hydrolyses it with the formation of dextrose and an amorphous, maroon-coloured substance not identical with gentiogenin.

T. A. H.

Caryophyllin. JOHANNES HERZOG (*Chem. Centr.*, 1905, ii, 553—554; from *Ber. Deut. pharm. Ges.*, 15, 121—124. Compare Meyer and Hönigschmid, this vol., i, 456).—Caryophyllin and diphenylcarbamate interact in pyridine solution to form *caryophyllin diphenylcarbamate*, $C_{40}H_{63}O_4 \cdot CO \cdot NPh_2$, which crystallises in needles, melts at $137-138^\circ$, and when hydrolysed yields caryophyllin and diphenylamine. When heated with acetic anhydride and sodium acetate, caryophyllin forms a *diacetyl* derivative, $C_{40}H_{62}O_4Ac_2$, which becomes brown at 210° and is completely melted at 255° . The composition of these derivatives is in agreement with caryophyllin, having the formula $C_{40}H_{64}O_4$, which requires C=78.9 per cent., but caryophyllin, when dissolved in cold alcohol, leaves a brown, insoluble residue, and the product from the solution, as also caryophyllin which has been purified by sublimation, contains C=75.7 per cent. The *potassium* and *barium* salts are described. The crystalline *benzoyl* derivative formed by heating caryophyllin and benzoic anhydride at 200° sinters at 173° and is melted at 185° . The *product* obtained on oxidation of caryophyllin with chromic acid in acetic acid solution at 80° is insoluble in aqueous sodium hydroxide, but dissolves in water, and forms an *oxime* and a *semicarbazone*.

G. Y.

Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1905, 38, 2712—2713. Compare Jackson and Menke, *Abstr.*, 1882, 1107).—Results of molecular weight determinations and of analyses are given which are in agreement with the formula, $C_{14}H_{14}O_4$, previously ascribed (*loc. cit.*) to curcumin. Ciamician and Silber's formula, $C_{21}H_{20}O_6$ (*Abstr.*, 1897, i, 229), was founded on the results of methoxyl determinations, which must be due to abnormal behaviour of curcumin with hydriodic acid.

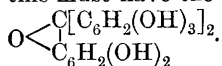
G. Y.

Rosocyanin. C. LORING JACKSON and LATHAM CLARKE (*Ber.*, 1905, 38, 2711—2712. Compare Schlumberger, *Bull. Soc. chim.*, 1866, [ii], 5, 194; Gajewsky, this Journal, 1873, 504, 760).—Rosocyanin, $C_{14}H_{14}O_4$, prepared by heating a mixture of curcumin, boric and sulphuric acids, alcohol, and water on the water-bath, is precipitated, on addition of ether to its rose-coloured, alcoholic solution, as a purplish-red substance, resembling powdered rosaniline, but with a slightly more yellow sheen. The *ammonium*, $C_{14}H_{13}O_4NH_4$, and the *potassium*, $C_{14}H_{13}O_4K$, salts are intensely blue.

G. Y.

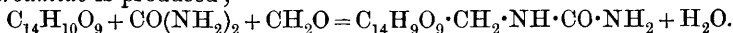
Preparation of Crystalline Gentiogenin. HENRI HÉRISSEY (*J. Pharm. Chim.*, 1905, [vi], 22, 249—251).—A claim for priority against Tanret (compare Hérissé and Bourquelot, *Abstr.*, 1900, i, 511; 1901, i, 258; ii, 34; and Tanret, this vol., i, 655). M. A. W.

The Carbonyl Group as Tannophore. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1905, ii, 659; from *Collegium*, 1905, 221—222. Compare Baeyer, this Journal, 1873, 501; Caro, *Abstr.*, 1893, i, 274; Kahl, *Abstr.*, 1898, i, 258).—The action of formaldehyde on gallic acid leads to the formation of hexahydroxydiphenylmethanedicarboxylic acid and Caro's hexahydroxyaurincarboxylic acid (*loc. cit.*), which is soluble in water and precipitates gelatin from its aqueous solution. Similarly from formaldehyde and pyrogallol there are obtained hexahydroxydiphenylmethane and a substance which is soluble in water and precipitates gelatin; this must have the constitution



The author considers that these facts support his view that the carbonyl group is the tannophore in the tannins. G. Y.

Condensation Products from Tannin, Formaldehyde, and Carbamide or Carbamates. ARNOLD VOSWINKEL (D.R.-P., 160273).—On addition of formaldehyde to an aqueous solution of tannin and carbamide in molecular proportions, a precipitate of *methylenetannin-carbamide* is produced;



The product is a yellow powder, becoming brown at 220° and then decomposing; it is insoluble in organic solvents with the exception of alcohol, and does not give the biuret reaction.

Carbamates react in similar manner. Thus tannin, ethyl carbamate, and formaldehyde yield the compound $\text{C}_{14}\text{H}_9\text{O}_9 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, which becomes brown and decomposes at 190°, and dissolves in alcohol and alkaline solutions. C. H. D.

Tannins producing a "Bloom" [on Leather]. II. MAXIMILIAN NIERENSTEIN (*Chem. Centr.*, 1905, ii, 527; from *Collegium*, 1905, 197—200. Compare this vol., i, 365).—Algarobilla (*Casalpinia brevifolia*) and divi-divi (*C. coriaria*) contain about 40—45 per cent. of pyrogallol tannins, which produce a light-coloured leather that appears blue in section; the blue colour is most probably caused by methyl gallate, which with excess of milk of lime gives a deep blue colour that remains permanent in the leather where it is not exposed, but disappears on exposure to air, forming a colourless, calcium salt. One hundred and forty-five grams of algarobilla husks were extracted with 4 litres of water; after three days, 20 grams of crude ellagic acid separated. The alcoholic mother liquors contained a substance which, on fusion with potassium hydroxide at 185°, yielded phloroglucinol and gallic acid. Tetra-acetyl ellagic acid melts at 311—313°, and not at 276—279° as previously stated. The aqueous filtrate from the ellagic acid contained *methyl gallate*, $\text{C}_8\text{H}_8\text{O}_5$, which separates from water in small crystals and melts at 189—190°; it gives a blue coloration with

ferric chloride, and also with lime-water, as above described; the aqueous filtrate yielded tannin glucoside, a glassy substance melting at $217-221^{\circ}$ (compare A. G. Perkin, *Trans.*, 1897, **71** 1135), which gives an acetyl derivative melting at 127° . P. H.

γ -Hydroxypyrrone and some of its Derivatives. I. Non-nitrogenous Derivatives. ALBERTO PERATONER (*Chem. Centr.*, 1905, ii, 678; from *Giorn. Sci. Nat. Econ.*, **25**, 239—244. Compare Peratoner and Leonardi, *Abstr.*, 1900, i, 550).—A theoretical introduction to the following five communications. G. Y.

Constitution of Comenic Acid. ALBERTO PERATONER and F. CARLO PALAZZO (*Chem. Centr.*, 1905, ii, 678; from *Giorn. Sci. Nat. Econ.*, **25**, 245—251).—Ostwald has shown that the introduction of a hydroxyl group in the ortho- or meta-position raises, but in the para-position depresses, the dissociation constant. Comenic acid (pyrone-2-carboxylic acid: Haitinger and Lieben, *Abstr.*, 1885, 965) has the dissociation constant $K=2.8$, whilst comenic acid has $K=2.0$, and is therefore 3-hydroxy- γ -pyrone-6-carboxylic acid. This conclusion is in agreement with the properties of comanamic and comenamic acids, which are weak acids and have the dissociation constants $K=0.0266$ and 0.0241 respectively (compare Ost, *Abstr.*, 1885, 49). G. Y.

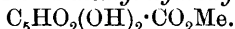
Alkyl Ethers of Pyromeconic Acids. ALBERTO PERATONER and ROSARIO SPALLINO (*Chem. Centr.*, 1905, ii, 678—679; from *Giorn. Sci. Nat. Econ.*, **25**, 252—258).—The constitution previously assumed for pyromeconic acid (Peratoner and Leonardi, *Abstr.*, 1900, i, 550) is confirmed by the formation of 3-ethoxy- γ -pyrone (Olivieri-Tortorici, *Abstr.*, 1902, i, 302) by the action of diazoethane on the acid.

The action of diazomethane on pyromeconic acid leads to the formation of 3-methoxy- γ -pyrone, $\text{CH} \begin{smallmatrix} \text{O}-\text{CH} \\ \text{CH} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{OMe}$, which crystallises from a mixture of petroleum and benzene, sublimes in a vacuum at $100-110^{\circ}$ in hard, colourless scales, melts at 85° , and when hydrolysed with calcium oxide yields formic acid and acetylcarbinol methyl ether (Leonardi and de Franchis, *Abstr.*, 1903, i, 787).

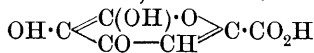
This reaction forms a general method for the determination of the constitution of simple hydroxy-derivatives of γ -pyrone, as on methylation with diazomethane and subsequent hydrolysis, those derivatives which have one or two hydroxyl groups in neighbouring positions to the carbonyl must yield acetylcarbinol methyl ether or the methyl ether of dihydroxyacetone, which are identified best as the *p*-nitrophenylhydrazones. G. Y.

Constitution of Hydroxycomenic Acid (Dihydroxypyrrone-carboxylic Acid). ALBERTO PERATONER and V. CASTELLANA (*Chem. Centr.*, 1905, ii, 679—680; from *Giorn. Sci. Nat. Econ.*, **25**, 259—271. Compare Tickle and Collie, *Trans.*, 1902, **81**, 1004).—Bromocomenic acid is prepared best by adding 1 mol. of bromine in acetic acid solution to 1 mol. of meconic acid dissolved in acetic acid and

evaporating the mixture under reduced pressure, or by subjecting powdered meconic acid to the action of bromine vapour for 36—48 hours. When boiled with dilute hydrochloric acid in a reflux apparatus, it is converted into hydroxycomenic acid, which, when acted on by hydrogen chloride in methyl-alcoholic solution at the laboratory temperature, forms *methyl hydroxycomenate*,



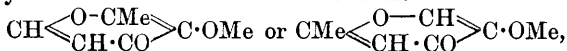
This crystallises in slender, white needles, melts at 222° , is easily hydrolysed by boiling water, and gives a red coloration with traces, or a blue coloration with excess, of ferric chloride. *Methyl dimethoxy- γ -pyronecarboxylate*, $\text{C}_5\text{HO}_2(\text{OMe})_2\cdot\text{CO}_2\text{Me}$, formed by the action of diazomethane on the methyl dihydroxy-ester in ethereal solution, crystallises in long, colourless needles, melts at 97° , and when boiled with very dilute hydrochloric acid yields *dimethoxy- γ -pyronecarboxylic acid*, $\text{C}_5\text{HO}_2(\text{OMe})_2\cdot\text{CO}_2\text{H}$, which crystallises in glistening scales and melts at 242° . When hydrolysed with baryta, the methyl dimethoxy-ester yields 1 mol. each of acetylcarbinol methyl ether, carbon dioxide, and oxalic acid, and 2 mols. of methyl alcohol; the methoxy-groups are therefore in the positions 2 and 3, and the constitution



for hydroxycomenic acid is confirmed.

G. Y.

Constitution of Maltol. ALBERTO PERATONER and ANTONIO TAMBURELLO (*Chem. Centr.*, 1905, ii, 680; from *Giorn. Sci. Nat. Econ.*, 25, 272—289. Compare Abstr., 1904, i, 61).—Maltol reacts with phenylcarbimide to form the *phenylcarbamate*, $\text{C}_5\text{H}_2\text{O}_2\text{Me}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, which crystallises in rosettes of hard needles, melts at $149\text{--}150^\circ$, and sublimes. The *methyl ether* of maltol, $\text{C}_5\text{H}_2\text{O}_2\text{Me}\cdot\text{OMe}$, formed by adding powdered dry maltol to an ethereal solution of diazomethane, is a colourless oil which boils at 114° under 15 mm. pressure, and in presence of even traces of impurities rapidly becomes red. When hydrolysed with baryta, it yields 1 mol. each of acetylcarbinol methyl ether and formic and acetic acids. Methyl alcohol is detected amongst the hydrolysis products by shaking the solution with freshly precipitated platinum black and adding phloroglucinol and potassium hydroxide solutions to the filtrate, when the characteristic red colour is obtained. The methyl ether has therefore the constitution



of which only the former can correspond to maltol, as this does not react with amyl nitrite or with diazonium acetate, sulphuryl chloride, and iodic acid (compare Peratoner, Abstr., 1902, i, 421), showing that it has the constitution which does not allow of change into the ketonic modification.

G. Y.

Pyridones from Pyromeconic Acid and Maltol. ALBERTO PERATONER and ANTONIO TAMBURELLO (*Chem. Centr.*, 1905, ii, 680—681; from *Giorn. Sci. Nat. Econ.*, 25, 290—297).—When heated with dilute ammonia and evaporated to dryness on the water-bath,

the alkyl ethers of pyromeconic acid and maltol are converted into the corresponding alkoxy-pyridones.

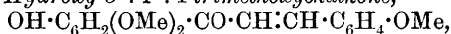
3-Methoxy-4-pyridone, $C_6H_7O_2N \cdot 3H_2O$, prepared from methyl pyromeconate, crystallises in small, glistening needles, melts at 114° , loses $3H_2O$ on prolonged heating at 100° , melts when anhydrous at 173° , sublimes in a vacuum at about 200° , gives an intense yellow coloration with ferric chloride, and when boiled with hydriodic acid yields 3-hydroxy-4-pyridone (pyrocomenamic acid: Ost, Abstr., 1883, 792).

3-Ethoxy-4-pyridone, $C_7H_9O_2N \cdot H_2O$, crystallises in rosettes of glistening plates, melts when quickly heated at $112-113^\circ$, or after prolonged heating at 100° , or drying over sulphuric acid in a vacuum at $135-136^\circ$, sublimes in a vacuum, gives a yellow coloration with ferric chloride, and by boiling hydriodic acid is converted into 3-hydroxy-4-pyridone.

3-Methoxy-2-methyl-4-pyridone, $C_7H_9O_2N$, formed from maltol, crystallises in small, hard, glistening needles, melts at 149° , sublimes in a vacuum at 220° , gives an intense yellow coloration with ferric chloride, and is converted by boiling hydriodic acid into 3:4-dihydroxy-2-methylpyridine hydriodide, which crystallises in white, glistening leaflets. The free base, $C_6H_7O_2N$, crystallises in small, hard, glistening needles, decomposes at about 250° , sublimes in a vacuum, and gives with ferric chloride a red coloration, which on addition of more ferric chloride becomes violet and finally blue. The *acetyl* derivative, $C_8H_6O_2N \cdot Ac$, crystallises in hard, glistening needles, melts at $204-205^\circ$, and sublimes.

The *acetyl* derivative of 3-hydroxy-4-pyridone, $C_7H_7O_3N$, crystallises in hard needles and melts at $207-208^\circ$. G. Y.

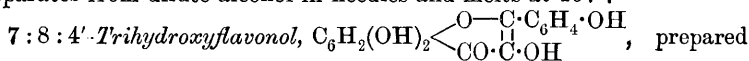
An Isomeride of Kaempferol. STANISLAUS VON KOSTANECKI and B. SCHREIBER (*Ber.*, 1905, **38**, 2748—2751. Compare Abstr., 1904, i, 607, 683).—2'-Hydroxy-3':4':4-trimethoxychalkone,



prepared by the condensation of gallacetophenone dimethyl ether with anisaldehyde, separates from alcohol in yellow plates and melts at $131-132^\circ$. The *acetyl* derivative forms pale yellow needles and melts at $89-90^\circ$.

7:8:4'-Trimethoxyflavanone, $C_{18}H_{18}O_5$, forms white needles and melts at 115° . Its isonitroso-derivative separates from benzene in pale yellow leaflets and melts and decomposes at 152° . It yields a brownish-yellow shade with cobalt mordants.

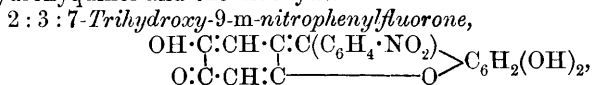
7:8:4'-Trimethoxyflavonol, $C_{18}H_{18}O_6$, forms pale yellow needles and melts at 198° . It forms a yellow sodium salt and produces a pale yellow shade with aluminium mordants. Its *acetyl* derivative separates from dilute alcohol in needles and melts at 157° .



from the trimethoxyflavonol by boiling with concentrated hydriodic acid, separates from alcohol in yellow needles and melts and decomposes at 319° . It dissolves in sodium hydroxide to an orange solution. It yields orange shades with aluminium mordants. Its

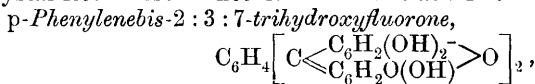
acetyl derivative separates from dilute alcohol in needles and melts at 175° . A. McK.

Condensation of Hydroxyquinol with Aldehydes. ERWIN HEINTSCHEL (*Ber.*, 1905, **38**, 2878—2883. Compare Liebermann and Lindenbaum, *Abstr.*, 1904, i, 443, 764).—The following fluorones, which melt above 300° , were obtained in the form of their sulphates by adding 15 per cent. sulphuric acid to an alcoholic solution of hydroxyquinol and the aldehyde.



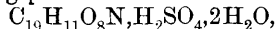
from *m*-nitrobenzaldehyde and hydroxyquinol, crystallises in small, metallic, reddish-brown prisms, is sparingly soluble in glacial acetic acid, alcohol, or acetone, forming solutions with yellowish-green fluorescence, and dissolves in aqueous alkali hydroxides to form bluish-red solutions. The *sulphate*, $\text{C}_{19}\text{H}_{11}\text{O}_7\text{N}\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$, forms brown, metallic needles and yields the free dye on addition of boiling water to its solution in alcohol containing a few drops of sulphuric acid. The *acetyl* derivative, $\text{C}_{25}\text{H}_{17}\text{O}_{10}\text{N}$, crystallises in orange needles and melts at 184° .

2 : 3 : 7-Trihydroxy-9-*m*-bromophenylfluorone, $\text{C}_{19}\text{H}_{11}\text{O}_6\text{Br}$, from *m*-bromobenzaldehyde and hydroxyquinol, forms glistening, scarlet prisms. The *sulphate*, $\text{C}_{19}\text{H}_{11}\text{O}_6\text{Br}\cdot\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$, forms brown, metallic needles and loses $3\text{H}_2\text{O}$ at 110° . The *acetyl* derivative, $\text{C}_{25}\text{H}_{17}\text{O}_8\text{Br}$, crystallises in brown needles and melts at 242° .



formed from terephthalaldehyde and hydroxyquinol, crystallises in dark brown, microscopic needles and is sparingly soluble in boiling nitrobenzene. The *sulphate*, $3\text{C}_{32}\text{H}_{18}\text{O}_{10}\cdot 2\text{H}_2\text{SO}_4\cdot 9\text{H}_2\text{O}$, forms dark brown, microscopic needles and yields the free dye on repeated boiling with alcohol and water. The *acetyl* derivative, $\text{C}_{41}\text{H}_{30}\text{O}_{16}$, forms a brown, crystalline powder and melts above 300° .

2 : 3 : 7-Trihydroxy-9-5'-nitro-2'-hydroxyphenylfluorone, $\text{C}_{19}\text{H}_{11}\text{O}_8\text{N}$, crystallises in glistening prisms or cubes. The *sulphate*,



forms brown, microscopic needles; the *acetyl* derivative, $\text{C}_{27}\text{H}_{19}\text{O}_{12}\text{N}$, crystallises in orange-red needles and melts at 193° .

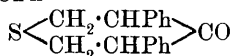
The fluorone *sulphate* obtained from 5-bromosalicylaldehyde forms red prisms mixed with a small quantity of colourless leaflets; the free *base* contains less bromine than is required for the formula $\text{C}_{19}\text{H}_{11}\text{O}_6\text{Br}$. When boiled with zinc dust, sodium acetate, and acetic anhydride, it yields 2 : 3 : 6 : 7-tetra-acetoxy-9-*o*-acetoxyphenylxanthen, $\text{C}_{29}\text{H}_{24}\text{O}_4$, which is obtained also by simultaneous reduction and acetylation of 2 : 3 : 7-trihydroxy-9-*o*-hydroxyphenylfluorone. It forms a white, crystalline powder, and melts at 196° . The colourless leaflets obtained along with the sulphate are soluble in ether, and, on acetylation, yield 7-bromo-2 : 3-diacetoxyxanthen, $\text{C}_{17}\text{H}_{13}\text{O}_5\text{Br}$, which

forms feathery aggregates of colourless crystals, melts at 146° , and is moderately soluble in alcohol, acetone, glacial acetic acid, or benzene.

The *sulphate* obtained from 3:5-dibromosalicylaldehyde and hydroxyquinol crystallises in dichroic, bluish-red prisms and yields the *fluorone*, $C_{19}H_{11}O_6Br$. This, when boiled with zinc dust, sodium acetate, and acetic anhydride, forms 2:3:6:7-*tetra-acetoxy-9-2'-acetoxy-3'-bromophenylxanthen*, $C_{29}H_{23}O_{11}Br$, which melts at 210° . Along with the sulphate, there is formed a substance which crystallises in colourless leaflets, and on acetylation yields a *product*, $C_{17}H_{13}O_5Br$, melting at $242-243^{\circ}$. On prolonged simultaneous reduction and acetylation, this yields a halogen-free *product* which melts at 184° , and is not identical with Liebermann and Lindenbaum's diacetoxyxanthen.

When boiled for 10—12 hours with zinc dust, sodium acetate, and acetic anhydride, 5-bromosalicylaldehyde yields *o*-acetoxybenzaldehyde diacetate, melting at 101° . 3:5-Dibromosalicylaldehyde, when boiled for 8 hours with zinc dust, sodium acetate, and acetic anhydride, yields 3-bromo-2-acetoxybenzaldehyde diacetate, $C_{13}H_{13}O_6Br$, which crystallises in prisms and melts at 134° . G. Y.

Action of Carbon Disulphide and Potassium Hydroxide on Ketones. II. HERMANN APITZSCH (*Ber.*, 1905, 38, 2888—2899. Compare *Abstr.*, 1904, i, 510).—The results of analyses are quoted, showing that the orange compound previously described as 1-keto-2:6-diphenyl-4-thiophen-3:5-dithiol is 4-keto-3:5-diphenylpenthiophen-2:6-dithiol, $S < \begin{smallmatrix} C(SH):CPh \\ C(SH):CPh \end{smallmatrix} > CO$, yielding the compound



on reduction, and that the formulæ for the derivatives of the orange compound must be altered accordingly.

The following derivatives of penthiophen are formed in the same manner.

4-Keto-3:5-dimethylpenthiophen-2:6-dithiol, $C_7H_8OS_3$, formed from diethyl ketone, crystallises in long, orange prisms, melts and decomposes at 157° , and is easily soluble in ethyl acetate, hot alcohol, toluene, xylene, or ethylene dibromide, but only sparingly so in ether, benzene, chloroform, or cold alcohol. The *sodium* derivative, $C_7H_6OS_3Na_2$, forms yellow crystals, and in aqueous solution forms coloured precipitates with the salts of the heavy metals. The *dimethyl* ether, $C_9H_{12}OS_3$, forms long, colourless needles and melts at 123° ; the *diethyl* ether forms straw-coloured prisms and melts at 70° ; the *dibenzyl* ether, $C_{21}H_{20}OS_3$, crystallises in colourless, glistening needles and melts at $65.5-66^{\circ}$. The *diacetyl* ester, $C_{11}H_{12}O_3S_3$, crystallises in small, yellow needles, becomes red at 100° , and melts and decomposes at about $109-112^{\circ}$; the *dibenzoyl* ester, $C_{21}H_{16}O_3S_3$, crystallises from light petroleum and melts at 105° .

4-Keto-3-methylpenthiophen-2:6-dithiol, $C_6H_6OS_3$, formed from methyl ethyl ketone, crystallises in small, orange needles, and melts at $144.5-145^{\circ}$. The *sodium* derivative, $C_6H_4OS_3Na_2 \cdot 2C_2H_5O$, crystallises from alcohol in yellow nodules and forms coloured precipitates with

salts of the heavy metals in aqueous solution. The *dimethyl ether*, $C_8H_{10}OS_3$, crystallises in yellow needles and melts at 89.5° . The *diacetyl ester*, $C_{10}H_{10}O_3S_3$, forms red needles and melts at $85.5-86^\circ$.

4-*Keto-3:5-diethylpenthiophen-2:6-dithiol*, $C_9H_{12}OS_3$, formed in small yield from dipropyl ketone, crystallises from chloroform and light petroleum in orange needles and melts at 118° .

4-*Keto-3-phenylpenthiophen-2:6-dithiol*, $C_{11}H_8OS_3$, formed from benzyl methyl ketone, crystallises in slender needles and melts at 135° .

4-*Keto-3-phenyl-5-methylpenthiophen-2:6-dithiol*, $C_{12}H_{10}OS_3$, formed from benzyl ethyl ketone, separates from acetone and light petroleum in red crystals and melts at 146° .

The action of carbon disulphide and potassium hydroxide on acetone leads to the formation of a red, amorphous *product* which could not be purified. G. Y.

Quinine Salts and Ammonium Salts. P. GUIGUES (*J. Pharm. Chim.*, 1905, [vi], 22, 303—306).—In an earlier paper (compare *Bull. trav. Soc. Pharm., Bordeaux*, December, 1900), the author pointed out that the crystallisation of quinine arsenate is accelerated by the addition of ammonium arsenate to the solution, and in the present paper he shows that the reaction is a general one, for if to a solution of quinine sulphate containing a little free sulphuric acid a solution of an ammonium salt (acetate, arsenate, arsenite, borate, bromide, carbonate, chloride, citrate, glycerophosphate, lactate, oxalate, phosphate, tartrate, valerate) is added, a mixture of quinine sulphate and the quinine salt of the other acid separates readily in a crystalline form; whereas, if the quinine sulphate is dissolved in acetic, citric, hydrochloric, lactic, phosphoric, tartaric, or valeric acid and the corresponding ammonium salt added, the quinine salt of the acid separates readily in a crystalline form and in a state of purity.

M. A. W.

Derivatives of Meroquinine. I. PAUL RABE and KARL RITTER (*Ber.*, 1905, 38, 2770—2773).—Cinchinonic acid and the *nitrile* of *methylmeroquinine* are obtained from von Miller and Rhode's *isonitrosomethylcinchotoxine* (Abstr., 1901, i, 95; compare Rabe and Denham, Abstr., 1904, i, 517; Rhode and Schwob, this vol., i, 228) by the Beckmann decomposition.

The nitrile, $CH_2 < \begin{smallmatrix} NMe \cdot CH_2 \cdot CH_2 \\ CH(CH=CH_2) \end{smallmatrix} > CH \cdot CH_2 \cdot CN$, has strongly basic properties and is volatile in steam. It is a colourless oil with an odour of piperidine, and boils at $252-255^\circ$ under 741 mm. pressure. The *methiodide*, $C_{11}H_{19}N_2I$, decomposes at $264-265^\circ$. The *picrate* melts at $93-95^\circ$ and the *picrotonate*, $C_{20}H_{24}O_5N_6$, is sparingly soluble and crystallises from alcohol in prismatic needles, melting at $194-195^\circ$ and insoluble in ether. The *aurichloride*, $C_{10}H_{17}N_2AuCl_4$, melts at $121-123^\circ$. J. J. S.

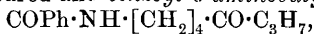
Separation of Conium Alkaloids. JULIUS VON BRAUN (*Ber.*, 1905, 38, 3108—3112. Compare Hofmann, Abstr., 1885, 562; Wolfenstein, *ibid.*, 1894, i, 627; 1895, i, 253).—The mixture of

alkaloids obtained from conium and containing *d*- and *l*-coniines, *d*- and *l*-methylconiines, γ -conicein, conhydrine, and ψ -conhydrine may be separated by the following method. The mixture is distilled and the portion passing over below 190° collected. The residue solidifies and, after crystallisation from ether, consists of pure conhydrine. The distillate is benzoylated, the product dissolved in ether, and any tertiary base removed by shaking with dilute acid. The ethereal solution is evaporated and the residue mixed with light petroleum. Benzoylconiine goes into solution and a considerable portion of the benzoyl-4-aminobutyl propyl ketone (from coniceine, see following abstract) remains undissolved. The light petroleum solution is evaporated and the residue distilled under reduced pressure. Benzoylconiine passes over at 200 – 210° under 16 mm. pressure, and the rest of the benzoylated ketone is left in the flask. The amounts of products obtained from 104 grams of mixture were: conhydrine 1, tertiary base 7, benzoylaminobutyl propyl ketone 52 (= coniceine 26), and benzoylconiine 124 (= coniine 68 grams).

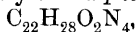
The tertiary base is a methylconiine. It distils at 176° under 751 mm. pressure, has a sp. gr. 0.7975 and $[\alpha]_D +35.66^{\circ}$ at 24° . The *picrate* melts at 114° , is sparingly soluble in hot water, but readily in alcohol. The *aurichloride* crystallises in yellow needles and melts at 82 – 90° . The relationship of these compounds to those described by Wolfenstein (*loc. cit.*) and Ahrens (Abstr., 1902, i, 390) has not been settled.

J. J. S.

γ -Coniceine. I. JULIUS VON BRAUN and ADOLF STEINDORFF (*Ber.*, 1905, 38, 3094–3107. Compare Hofmann, Abstr., 1885, 562; Lellmann, *ibid.*, 1889, 901; 1890, 1328; Wolfenstein, *ibid.*, 1895, i, 253, 479).—When benzoylated by the Schotten-Baumann method, the ring of γ -coniceine is ruptured and *benzoyl- δ -aminobutyl propyl ketone*,



is formed. It crystallises from warm water in slender needles, or from a mixture of ether and light petroleum in prisms, and dissolves in most organic solvents. It yields a *phenylsemicarbazone*,



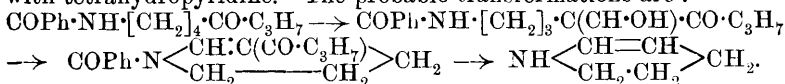
melting at 150° and sparingly soluble in cold alcohol. Other acyl chlorides react similarly to benzoyl chloride. *Anisoylaminobutyl-propyl ketone*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot [\text{CH}_2]_4 \cdot \text{CO} \cdot \text{C}_3\text{H}_7$, crystallises from warm ether and melts at 80° . The *semicarbazone*, $\text{C}_{17}\text{H}_{26}\text{O}_3\text{N}_4$, melts at 144° ; the *oxime* crystallises in colourless plates melting at 123° .

Both the benzoyl and anisoyl derivatives, when hydrolysed with concentrated hydrochloric acid at 120° , yield coniceine and the corresponding acid. Coniceine *picrate* melts at 72 – 73° ; Wolfenstein gives 62° .

Coniceine, after purification by distillation in steam, does not give the characteristic greenish-red coloration when its solution in hydrochloric acid is evaporated; whereas the base, which has been purified by distillation under atmospheric pressure, gives an intense colour.

The benzoyl derivative condenses with sodium and ethyl acetate or oxalate yielding oily products. With sodium and amyl formate and subsequent addition of acid, an *oil*, $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$, distilling at

230—235° under 15 mm. pressure is obtained. It is not an oxymethylene compound, as it does not give any coloration with ferric chloride. Its *semicarbazone* melts at 190°, and when heated for several hours with concentrated acids yields benzoic and butyric acids together with tetrahydropyridine. The probable transformations are :

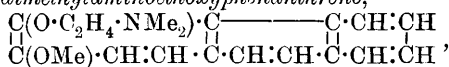


Coniceine yields an *additive compound* with benzaldehyde in the form of a reddish-yellow oil, soluble in ether, alcohol, or dilute acids. The acid solution is pale yellowish-red, but gradually assumes a green colour. The *platinichloride* of the additive compound decomposes at 155° and the *aurichloride* forms a yellow precipitate which rapidly sets to a resin.

Coniceine and nitrous acid yield nitrogen and a compound, $\text{C}_8\text{H}_{14}\text{O}$, boiling at 150°. The behaviour of coniceine towards benzoyl chloride, taken in conjunction with Lipp's experiments on tetrahydropicoline (Abstr., 1896, i, 317) and Wallach's on a similar base (*Annalen*, 1899, 309, 28; 1901, 319, 104), indicate that the grouping $>\text{N}\cdot\text{C}:\text{C}:$ in a ring is unstable, the ring showing a great tendency to rupture. J. J. S.

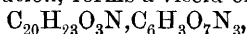
Synthetical Bases from Methylmorphol and Thebaol and their Behaviour towards Reagents which Decompose Methylmorphimethine. LUDWIG KNORR (*Ber.*, 1905, 38, 3143—3153. Compare Abstr., 1889, 1218).—*Phenyl dimethylaminoethyl ether*, $\text{C}_{10}\text{H}_{15}\text{ON}$, formed when dimethylchloroethylamine and phenol are heated with sodium ethoxide in alcoholic solution at 120°, boils at 232° under 750 mm. pressure, has a slight odour, and is easily soluble in alcohol or ether; the *aurichloride*, $\text{C}_{10}\text{H}_{15}\text{ON}\cdot\text{HAuCl}_4$, forms glistening, yellowish-red leaflets and melts at 124—125°.

3-Methoxy-4-dimethylaminoethoxyphenanthrene,



is formed when dimethylchloroethylamine hydrochloride and methylmorphol are heated with sodium ethoxide in alcoholic solution, in an atmosphere of nitrogen, in a sealed tube at 150—160°. It is obtained as a colourless, viscid oil, which is easily soluble in alcohol and ether; the *hydrochloride*, $\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}\cdot\text{HCl}$, crystallises in silvery leaflets and melts at 214—215°; the *picrate* crystallises in slender, yellow needles and melts at 189°; the crystalline *methiodide*, $\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}\cdot\text{MeI}$, melts at 196—198°. The base is not acted on by *N*-alcoholic sodium ethoxide at 150°, but is decomposed by hydrogen chloride, with formation of morphol, tetramethylethylenediamine, and dimethylaminoethyl alcohol, and when treated with acetic anhydride yields dimethylaminoethyl alcohol and acetylmethylmorphol.

3:6-Dimethoxy-4-dimethylaminoethoxyphenanthrene, $\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}$, obtained by heating thebaol with dimethylchloroethylamine and sodium ethoxide in alcoholic solution, forms a viscid oil; the *picrate*,



crystallises from boiling alcohol in matted, slender needles and melts at 186° ; the *methiodide*, $C_{30}H_{23}O_3N, MeI, 1\frac{1}{2}CH_4O$, crystallises in glistening leaflets, loses $1\frac{1}{2}CH_4O$ at 120° , and melts at $199-200^{\circ}$. The base is not acted on by *N*-alcoholic sodium ethoxide at 150° , but when heated with acetic anhydride at 170° yields acetylthebaol and ethanoldimethylamine.

These facts agree with the author's supposition that methylmorphine contains the group $-O \cdot C_2H_4 \cdot NMe_2$. G. Y.

Degradation of Morphothebaine to Non-nitrogenous Phenanthrene Derivatives. LUDWIG KNORR and ROBERT PSCHORR (*Ber.*, 1905, 38, 3153—3159. Compare Knorr, *Abstr.*, 1903, i, 849; Pschorr and Massaciu, *Abstr.*, 1904, i, 767).—*Tribenzoylmorphothebaine*, $C_{39}H_{31}O_6N, C_4H_{10}O$, formed by boiling morphothebaine hydrochloride with benzoyl chloride in a reflux apparatus, crystallises from a mixture of chloroform and ether and melts at 120° or, after loss of $C_4H_{10}O$, at 181° .

Dimethylthebainemethine methiodide, $C_{22}H_{28}O_3NI$, is formed by the action of sodium methoxide and methyl iodide on morphothebaine in methyl-alcoholic solution at 100° , or of methyl sulphate and sodium hydroxide on morphothebaine methiodide in aqueous solution at 100° . It forms shimmering leaflets, decomposes and melts at $266-268^{\circ}$, and when boiled with aqueous sodium hydroxide yields trimethylamine, trimethoxyvinylphenanthrene, and a grey, sandy powder, $(C_{19}H_{18}O_3)_x$, which sinters at $200-300^{\circ}$ and is sparingly soluble in most solvents. *Trimethoxyvinylphenanthrene*, $C_{16}H_9(OMe)_3$, obtained in this manner, separates from its alcoholic solution, on addition of water, as an oil which solidifies in prisms. It melts at $60-61^{\circ}$, dissolves in the usual organic solvents to form solutions with slight bluish-violet fluorescence, is not acted on by boiling glacial acetic acid, and is isomeric with the trimethoxyvinylphenanthrene obtained from thebinine, which must have the vinyl group in the ortho- or the meso-position. The *picrate*, $C_{19}H_{18}O_8, C_6H_3O_7N_3$, crystallises in reddish-violet needles and melts at $125-126^{\circ}$. The vinyl compound decolorises a chloroform solution of less than 1 mol. of bromine, and when oxidised with potassium permanganate in aqueous acetone solution yields a *trimethoxyphenanthrenecarboxylic acid*, $C_{18}H_{16}O_5$, which crystallises in slender, yellow needles, melts at 201° , and distils with only slight decomposition under 30 mm. pressure, yielding feathery crystals which melt at 181° ; on prolonged boiling in a reflux apparatus, it yields a viscous oil which is insoluble in aqueous alkali hydroxides and may be 3 : 4 : 6-trimethoxyphenanthrene.

A table is given showing the melting points of the derivatives obtained from morphothebaine and from thebinine; as both these are formed from thebaine, but yield isomeric derivatives, intramolecular change must take place in the formation or in the decomposition of at least one of the two bases. G. Y.

Esterification of Polyhydric Alcohols by Phosphoric and Phosphorous Acids. PAUL CARRÉ (*Ann. Chim. Phys.*, 1905, [viii], 5, 345—432).—A memoir giving a detailed account of work for the

most part already published (Abstr., 1902, i, 131, 338; 1903, i, 307, 405, 456, 598; 1904, i, 16, 133, 215, 281, 819, 974. Compare Power and Tutin, Trans., 1905, 87, 249). *Brucine glycylphosphate*, $\text{PO}(\text{OH})_2 \cdot \text{O} \cdot \text{C}_2\text{H}_5\text{O} \cdot (\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_1)_2 \cdot 12\text{H}_2\text{O}$, crystallises in small prisms, melts at 181° , and is soluble in warm water, less so in cold, and insoluble in ether. *Brucine hydrogen glycylphosphate* crystallises (with $3\text{H}_2\text{O}$) in needles, melts at 176° , and is readily soluble in water and alcohol. The neutral and basic quinine salts (Abstr., 1904, i, 282) melt at 169° and 123° respectively.

Brucine glycerolphosphate crystallises in needles with $9\text{H}_2\text{O}$, becomes anhydrous at 100° , melts at 181° , is soluble in alcohol or warm water, less so in cold water, and insoluble in ether. *Brucine hydrogen glycerolphosphate* crystallises from water in needles and melts at 176° .

Brucine erythritolphosphate crystallises from water in prisms (containing $12\text{H}_2\text{O}$), melts at 169° , and is very soluble in water or alcohol. The acid salt separates from its solution in water, on addition of acetone, in slender, efflorescent needles containing $4\text{H}_2\text{O}$, becomes anhydrous at 100° , and melts at 166° .

Quinine erythritolphosphate crystallises in slender needles and melts at 138° . *Quinine hydrogen erythritolphosphate* separates in needles which contain water of crystallisation, but the salt is efflorescent and rapidly becomes anhydrous, and then melts at 191° .

When dihydrogen erythritolphosphate (Abstr., 1903, i, 307) is warmed, it is converted into the *di-ester*, $\text{OH} \cdot \text{PO} \begin{array}{c} \text{O} \cdot \text{CH} \cdot \text{CH}_2 \\ | \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{O}$, which crystallises in small prisms, decomposes at 205° , is mono-acidic, and on solution in water is rapidly converted into the mono-ester.

Brucinemannide phosphate, $\text{PO}(\text{OH})_2 \cdot \text{O} \cdot \text{C}_6\text{H}_9\text{O}_3 \cdot (\text{C}_{23}\text{H}_{26}\text{O}_4\text{N}_2)_2 \cdot 10\text{H}_2\text{O}$, separates from its solutions in water on addition of acetone in clusters of slender needles and melts at 179° . The analogous *quinine* salt contains $2\text{H}_2\text{O}$, crystallises in needles, and melts at 136° . *Mannide diphenylurethane*, $\text{C}_6\text{H}_5\text{O}_4(\text{CO} \cdot \text{NHPh})_2$, crystallises in spangles and melts at 243° .

A general *résumé* of the author's results is given in the original.

T. A. H.

isoStrychnine. A. BACOVESCU and AMÉ PICTET (*Ber.*, 1905, 38, 2787—2792. Compare Gal and Étard, Abstr., 1879, 387; Tafel, Abstr., 1891, 1262).—*isoStrychnine*, obtained when strychnine is heated with water in a sealed tube at 160 — 180° , crystallises from hot water in prismatic needles containing $3\text{H}_2\text{O}$. It melts at 214.5° , is soluble in about 65 parts of hot water, sparingly in benzene or chloroform, and insoluble in ether, light petroleum, or alkalis, and is optically inactive. It gradually becomes brown in contact with acids or alkalis, and is probably identical with Gal and Étard's trihydrostrychnine. The anhydrous base, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$, crystallises from benzene in glistening needles melting at 214 — 215° . The *hydrochloride*, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$, melts and decomposes at about 314° . The *platinichloride* and *aurichloride* are pale yellow, amorphous precipitates. The *mercurichloride* is crystalline and melts at 228° , and the *picrate*, also crystalline, blackens at about 245° .

*iso*Strychnine gives a purple coloration with potassium dichromate and concentrated sulphuric acid, but this rapidly changes to yellow. With bromine water, it gives a pale yellow precipitate, and with warm ferric chloride solution a red coloration. With Mandelin's reagent, it gives a pale brown coloration, and also readily reduces gold, platinum, and silver salts. When boiled for six hours with sodium ethoxide solution, the base yields Tafel's *iso*strychnic acid.

It is not so strongly toxic as strychnine, and its physiological properties more closely resemble those of brucine than of strychnine.

J. J. S.

Strychnine Oxide. AMÉ PICTET and MAX MATTISSON (*Ber.*, 1905, 38, 2782—2787).—*Strychnine oxide*, $C_{21}H_{22}O_3N_2 \cdot 3H_2O$, is obtained when strychnine is warmed on the water-bath with 3 per cent. hydrogen peroxide solution. It crystallises in large, colourless, monoclinic prisms [$a : b : c = 2.1280 : 1 : 2.5300$] and has the properties of an aminoxide. Both in the hydrated and anhydrous states it melts and decomposes at 199° , and has $[a]_D - 1.75^\circ$. It is moderately soluble in cold water (at 22° , 10 c.c. of a saturated solution contain 0.1864 gram of anhydrous oxide); the solution is neutral and has a bitter taste. The oxide is insoluble in ether or light petroleum. It evolves oxygen when gently warmed, and liberates iodine from potassium iodide in the cold. Strychnine sulphate is formed when sulphur dioxide is passed into a concentrated aqueous solution of the oxide and the alkaloid is regenerated by the action of nitrous acid on the oxide.

The salts are sparingly soluble. The solutions are acid and do not yield precipitates with ammonia. The *hydrochloride*, $C_{21}H_{22}O_3N_2 \cdot HCl$, crystallises in long, glistening needles, darkens at 250° , but is still solid at 310° . The *platinichloride* forms flat needles and is insoluble in water. The *hydriodide* forms pale yellow, quadratic plates and melts and decomposes at 253° ; it forms reddish-yellow periodides. The *nitrate* crystallises in prisms and melts and decomposes at about 250° ; the *picrate* melts and decomposes at 208° ; the *hydrogen sulphate* crystallises in large, four-sided plates, is somewhat more soluble in water than the other salts, and melts above 300° .

Methyl iodide reacts with the oxide yielding strychnine methiodide.

The physiological action is very similar to that of the alkaloid.

The conclusion is drawn that the nitrogen atom in strychnine to which the oxygen becomes attached must be linked to three distinct carbon atoms, and these are contained in two ring systems, since no alkyl group appears to be attached to the nitrogen (compare Freund, *Abstr.*, 1904, i, 613). Brucine also yields a crystalline oxide.

J. J. S.

Yohimbine. II. Methylation of Yohimboic Acid. LEOPOLD SPIEGEL (*Ber.*, 1905, 38, 2825—2833. Compare Spiegel and Auerbach, *Abstr.*, 1904, i, 521).—The action of diazomethane on yohimboic acid leads to the formation of yohimboic anhydride and *yohimbine yohimboate*, which melts at 120 — 125° and on treatment with ammonia yields yohimbine. If an excess of diazomethane is used, the yohim-

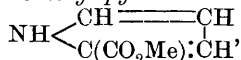
boaic acid is converted completely into yohimbine. The *anhydride*, $C_{20}H_{24}O_3N_2$, which is formed also by the action of methyl or ethyl alcohol on the acid, crystallises from alcohol and melts at 296° ; on exposure to the air, it changes into a crystalline powder which melts, when rapidly heated, at 249° . It can be recrystallised almost unchanged from hot ammonia, but if recrystallised from hot water or slowly evaporated in ammoniacal solution, yields the acid. When treated with ethyl-alcoholic hydrogen chloride, the anhydride forms a crystalline hydrochloride which, on treatment with ammonia, yields ethlyyohimbine melting at 189° , but treatment with methyl-alcoholic hydrochloric acid leads to the formation of yohimbine melting at 231° .

Methlyyohimboaic acid, $C_9NH_{12} \cdot CO \cdot O \cdot C_9NH_{12}Me \cdot CO_2H$, formed by the action of methyl sulphate or of methyl iodide and sodium hydroxide on yohimboaic acid in *N*-potassium hydroxide solution, separates in colourless crystals, melts at 293 – 294° , and is easily soluble in hydrochloric or acetic acid to form solutions from which addition of an excess of sodium hydroxide precipitates the *sodium* salt; the aqueous solution of this deposits the free acid when the walls of the glass vessel are rubbed with a rod, as does also the solution of the acid in aqueous ammonia. The ammoniacal mother liquor on concentration deposits yohimboaic acid and a *substance* which forms large crystals, melts at 254° , and is a compound of yohimboaic and methlyyohimboaic acids. When treated with hydrogen chloride in alcoholic solution, methlyyohimboaic acid yields on evaporation a viscous *substance* which is converted into methlyyohimboaic acid when treated with sodium hydroxide. The action of ethyl sulphate on yohimboaic acid leads to the formation of *ethlyyohimboaic acid*, $C_{22}H_{30}O_4N_2$, which melts at 250° .
G. Y.

Chloropyrrole and Chlorotribromopyrrole. X. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, 35, ii, 19–27. Compare this vol., i, 659).—2-Chloro-3:4:5-tribromo-1-methylpyrrole,

$NMe \begin{matrix} \text{CCl} : CBr \\ \diagup \quad \diagdown \\ CBr : CBr \end{matrix}$, obtained by the action of methyl-alcoholic potassium hydroxide and methyl iodide on a methyl-alcoholic solution of chlorotribromopyrrole, crystallises from alcohol in long, faintly pearly-grey needles melting at 138° , and is stable towards the action of light. On oxidation with concentrated nitric acid, it yields dibromomaleinmethylimide, so that chlorotribromopyrrole and also chloropyrrole must have the chlorine atom in the 2-position.
T. H. P.

Action of Sulphuryl Chloride on Methyl Pyrrole-2-carboxylate. XI. GIROLAMO MAZZARA and ALESSANDRO BORGO (*Gazzetta*, 1905, 35, ii, 104–111).—*Methyl pyrrole-2-carboxylate*,



prepared from the corresponding ammonium salt obtained by heating together ammonium carbonate, pyrrole, and water under pressure, crystallises in shining, white needles melting at 73° .

Methyl-3 : 4 : 5-trichloropyrrole-2-carboxylate, $\text{NH} \begin{array}{l} \text{CCl}=\text{CCl} \\ \text{C}(\text{CO}_2\text{Me})\cdot\text{CCl} \end{array}$

prepared by the action of sulphuryl chloride (3 mols.) on an ethereal solution of methyl pyrrole-2-carboxylate (1 mol.), crystallises from alcohol in shining, white needles melting at 189° and is soluble in light petroleum. It is accompanied by *methyl dichloropyrrole-2-carboxylate*, $\text{C}_4\text{NH}_2\text{Cl}_2\cdot\text{CO}_2\text{Me}$, which can be obtained pure by using two mols. of sulphuryl chloride and one of methyl pyrrole-2-carboxylate; it crystallises from light petroleum in slender needles melting at $132\text{--}134^\circ$ and dissolves in water or alcohol.

Methyl chloropyrrole-2-carboxylate, $\text{C}_4\text{NH}_3\text{Cl}\cdot\text{CO}_2\text{Me}$, prepared by the interaction of sulphuryl chloride and methyl pyrrole-2-carboxylate in molecular proportions, was not obtained pure, but melts at about 90° . The corresponding *acid*, $\text{C}_4\text{NH}_3\text{Cl}\cdot\text{CO}_2\text{H}$, separates from water in faintly rose-coloured crystals which soften and decompose at about 130° .

T. H. P.

Cyclic Bases from Methylheptenone. OTTO WALLACH (*Ber.*, 1905, **38**, 2803—2806).—The additive compound of the base $\text{C}_8\text{H}_{15}\text{N}$ and benzaldehyde (*Abstr.*, 1902, i, 81) appears to be a benzhydrol, $\text{C}_8\text{H}_{14}\text{N}\cdot\text{CHPh}\cdot\text{OH}$, as it slowly decomposes into its components.

[With PETROS RHOSSOPOULOS.]—Methylheptenylamine combines with two molecules of hydrogen chloride or bromide, and the products, when distilled, yield a *hydrocarbon*, C_8H_{14} , boiling at 130° , and a base, $\text{CHMe}_2\cdot\text{CH} \begin{array}{l} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CHMe} \end{array}$ (?), isomeric with coniine. This distils at $150\text{--}151^\circ$, has a specific gravity 0.823, and n_D 1.4398 at 20° . The *hydrochloride* melts at $218\text{--}220^\circ$ and the *plutini chloride* at $221\text{--}223^\circ$. The *nitrosoamine* distils at 114° under 10 mm. pressure, and the *sulphonamide*, $\text{C}_8\text{H}_{16}\text{N}\cdot\text{SO}_3\text{Ph}$, melts at $76\text{--}78^\circ$. When completely methylated, it yields a *quaternary ammonium iodide*, $\text{C}_8\text{H}_{16}\text{NMe}_2\text{I}$, which melts at $242\text{--}243^\circ$.

Attention is drawn to the fact that a similar decomposition to that described by Lipp and Widmann (this vol., i, 610) has been previously observed with the base $\text{C}_8\text{H}_{15}\text{N}$.

J. J. S.

4-Stilbazole and 3'-Nitro-4-stilbazole. KONRAD FRIEDLÄNDER (*Ber.*, 1905, **38**, 2837—2840. Compare this vol., i, 232).—*Dihydro-4-stilbazole*, $\text{C}_5\text{NH}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, formed by heating 4-stilbazole with fuming hydriodic acid and red phosphorus in a sealed tube at 150° , crystallises in white needles and melts at 65° . The *hydrochloride*, $\text{C}_{13}\text{H}_{13}\text{N}\cdot\text{HCl}$, melts at about 180° ; the *hydriodide* crystallises in glistening, brown leaflets and decomposes at 150° ; the *aurichloride*, $\text{C}_{13}\text{H}_{13}\text{N}\cdot\text{HAuCl}_4$, forms leaflets and melts at 166° ; the *platinichloride*, $(\text{C}_{13}\text{H}_{13}\text{N})_2\cdot\text{H}_2\text{PtCl}_6$, forms brown leaflets and commences to melt slowly at 214° .

4-Stilbazoline, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, prepared by reduction of 4-stilbazole with sodium in alcoholic solution, forms a light oil which has an unpleasant odour and boils at $200\text{--}210^\circ$ under 80 mm. pressure. The *aurichloride*, $\text{C}_{13}\text{H}_{19}\text{N}\cdot\text{HAuCl}_4$, forms golden-red leaflets and melts

and decomposes at 204° ; the *platinichloride*, $(C_{13}H_{19}N)_2 \cdot H_2PtCl_6$, forms brown leaflets and melts at about 210° .

3'-Nitro-4-stilbazole, $C_5NH_4 \cdot CH:CH \cdot C_6H_4 \cdot NO_2$, formed by heating *m*-nitrobenzaldehyde and 4-methylpyridine in a sealed tube at 180 — 200° , crystallises from alcohol in brown needles and melts at 138° . The *hydrochloride*, $C_{13}H_{10}O_2N_2 \cdot HCl$, is a white powder melting at 221 — 222° ; the *picrate* forms explosive, yellowish-green crystals; the *platinichloride*, $(C_{13}H_{10}O_2N_2)_2 \cdot H_2PtCl_6$, crystallises in reddish-yellow leaflets and melts at a high temperature; the *aurichloride* forms a red powder and melts at a high temperature. Reduction of 3'-nitro-4-stilbazole with stannous chloride in alkaline solution leads to the formation of *azo-4-stilbazole*, $N_2(C_6H_4 \cdot CH:CH \cdot C_5NH_4)_2$, which forms small, red crystals and melts at 220 — 221° . 3'-Nitro-4-stilbazole is reduced electrolytically in concentrated sulphuric acid with a current density of $2\frac{1}{2}$ —3 amperes and an *E.M.F.* of 4 volts, with formation of 3'-amino-6'-hydroxy-4-stilbazole, $C_5H_4N \cdot CH:CH \cdot C_6H_3(NH_2) \cdot OH$, which separates from alcohol in small, glistening prisms and melts at 123° . 3'-Aminodihydro-4-stilbazole, $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$, is formed by reduction of 3'-nitro-4-stilbazole with fuming hydriodic acid and red phosphorus at 135 — 150° , or with tin and hydrochloric acid. It crystallises from alcohol in almost colourless needles and melts at 127 — 129° . G. Y.

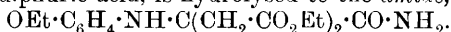
β -Aminotricarballylic Acid. GEORG SCHROETER (*Ber.*, 1905, **38**, 3181—3189. Compare Schroeter and Kirnberger, *Abstr.*, 1902, i, 531).—[With R. SCHWAMBORN and C. STASSEN.]— β -Anilino*tricarballylic acid*, $NHPh \cdot C(CH_2 \cdot CO_2H)_2 \cdot CO_2H \cdot H_2O$, is formed by boiling the ethyl ester of its imide (*loc. cit.*) with 12 per cent. aqueous sodium hydroxide and adding a limited quantity of hydrochloric acid to the product; if more dilute sodium hydroxide is used, the hydrolysis proceeds further with formation of aniline. The anilino-acid is obtained as a crystalline powder, melts and decomposes at 161 — 162° , or, after losing H_2O at 90° under reduced pressure, at 169° , and is slowly hydrolysed by boiling 10 per cent. hydrochloric acid with formation of aniline and probably aconitic acid. It neutralises almost three mols. of sodium hydroxide when titrated with phenolphthalein as indicator, but acts as a dibasic acid towards litmus in dilute solution; the concentrated solution of the *sodium* salt yields *precipitates* with salts of calcium, barium, or the heavy metals; on analysis, the *silver* and *barium* salts gave results corresponding with between two and three equivalents of metal per mol. of the acid.

The *imide* of aconitic acid, $\begin{array}{c} NH \cdot CO \\ | \quad \diagup \\ CO \cdot CH \end{array} \Rightarrow C \cdot CH_2 \cdot CO_2H$, is formed by boiling the ethyl ester of β -anilino*tricarballylimide* with 2*N*-hydrochloric acid in a reflux apparatus. It crystallises from hot water, melts at 191° , and neutralises more than one mol. of sodium hydroxide when titrated with phenolphthalein as indicator, but acts as a monobasic acid towards a mixture of potassium iodide and iodate; when boiled with aqueous sodium hydroxide, it is hydrolysed with formation of ammonia and aconitic acid. The *silver* salt, $C_6H_3O_4Na_2$, was

analysed. This substance is the *as*-imide as compared with citrazinic acid, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CO} - \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$, which is the *s*-imide of aconitic acid.

When boiled with hydrochloric acid, α -anilino- α -methylsuccinimide is hydrolysed with formation of citraconanil and a substance which melts at 145° .

[With R. SCHWAMBORN.]—A molecular mixture of ethyl acetonedicarboxylate and phenetidine interacts in two days to form *ethyl phenetidinil-acetonedicarboxylate*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2$, which crystallises from light petroleum in transparent prisms and melts at 57° . This dissolves in absolute hydrogen cyanide and, if after two to three days the excess of hydrogen cyanide is distilled off, forms the *nitrile*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2 \cdot \text{CN}$, which, when dissolved in cold concentrated sulphuric acid, is hydrolysed to the *amide*,



This crystallises from aqueous alcohol or from a mixture of chloroform or benzene and light petroleum and melts at 77° . Prolonged action of concentrated sulphuric acid on the nitrile leads to the formation of the

imide, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \cdot \text{CO} \begin{smallmatrix} \text{CH}_2 \text{-----} \text{CO} \end{smallmatrix} \text{NH}$, which crystallises from

alcohol, melts at $133\text{--}134^\circ$, and has stronger basic properties than has the imide of ethyl β -anilino-tricarballic acid. If the imide is dissolved in aqueous sodium hydroxide and the solution carefully acidified, the

imide-acid, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CO} \begin{smallmatrix} \text{CH}_2 \text{-----} \text{CO} \end{smallmatrix} \text{NH}$, is precipitated; it

crystallises from water, melts and decomposes at 153° , and forms a *disodium salt*, $\text{C}_{14}\text{H}_{14}\text{O}_5\text{N}_2\text{Na}_2$. β -Phenetidinotricarballic acid, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2 \cdot \text{CO}_2\text{H} \cdot 2\text{H}_2\text{O}$, is formed along with a small amount of phenetidine by boiling the imide-ester with *2N*-sodium hydroxide; it crystallises from water in small cubes, melts and decomposes at $121\text{--}122^\circ$, and loses $2\text{H}_2\text{O}$ at 55° under reduced pressure. When boiled with *2N*-hydrochloric acid, the ethyl ester of β -phenetidinotricarballic imide is hydrolysed to phenetidine and the *as*-imide of aconitic acid.

[With C. STASSEN.]—The following substances have been prepared from the toluidines in the same manner as the preceding; the temperatures given are melting points:

	<i>o</i> .	<i>m</i> .	<i>p</i> .
Ethyl toluidilacetonedicarboxylates	78°	59°	52°
The amides, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et})_2 \cdot \text{CO} \cdot \text{NH}_2$	$141\text{--}142^\circ$	104°	$79\text{--}80^\circ$
The imides, $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{C}(\text{CH}_2 \cdot \text{CO}_2\text{Et}) \cdot \text{CO} \begin{smallmatrix} \text{CH}_2 \text{-----} \text{CO} \end{smallmatrix} \text{NH}$	$90.5\text{--}91.5^\circ$	$135\text{--}136^\circ$	$208\text{--}209^\circ$

The imide from *m*-toluidine is hydrolysed by sodium hydroxide with formation of *m*-toluidinocarballic acid, which melts and decomposes at 152° , or by boiling hydrochloric acid with formation of *m*-toluidine and the *as*-imide of aconitic acid. The product obtained by treating with sulphuric acid the nitrile formed by condensation of ammonia, ethyl acetonedicarboxylate, and hydrogen cyanide is soluble in aqueous alkali hydroxides, and in neutral solution forms precipitates with solutions of

barium, copper, and silver salts. The *silver* salt so obtained gives on analysis results corresponding with a mixture of di- and tri-silver β -aminotricarballylates. G. Y.

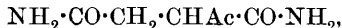
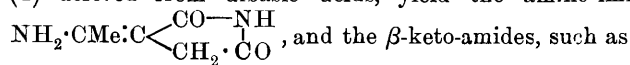
Piperidoethyl Ether. LUDWIG KNORR, H. HÖRLEIN, and PAUL ROTH (*Ber.*, 1905, **38**, 3141—3142. Compare preceding abstract).—*Piperidoethyl ether hydrochloride*, $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot OEt, HCl$, is formed along with diethylenedipiperidinium chloride when 1-chloroethyl-piperidine is boiled with alcohol (compare Marckwald and Frobenius, *Abstr.*, 1902, i, 24). The free *base*, $C_9H_{19}ON$, can be prepared by heating 1-chloroethylpiperidine hydrochloride with sodium ethoxide in alcoholic solution in a sealed tube; it forms an oil which boils at 196° under 760 mm. pressure. The *aurichloride*, $C_9H_{19}ON, HAuCl_4$, forms an oil which rapidly crystallises and melts at about 85° ; the *platinichloride* crystallises in flat, monoclinic prisms and melts at 116 — 117° ; the *picrate* is an oil; the *picrolonate* crystallises in characteristic, fan-like aggregates of leaflets. G. Y.

Simple Method for the Preparation of Pyridine Perchromate for Demonstration Purposes. KARL A. HOFMANN and H. HIENDLMAIER (*Ber.*, 1905, **38**, 3066—3067. Compare Wiede, *Abstr.*, 1898, ii, 28).—Pyridine perchromate, CrO_5H, C_5H_5N , may be prepared by the following method. Chromic anhydride (4 grams) is dissolved in water (150 c.c.) and mixed with pyridine (9 c.c.). To this solution, which is kept cool by a good freezing mixture, 30 per cent. hydrogen peroxide (4 c.c.) dissolved in water (20 c.c.) is added. The perchromate separates as dark blue, glistening needles, practically insoluble in water, but dissolves readily in ether or glacial acetic acid. J. J. S.

Synthesis of Pyridine Compounds from β -Keto-esters and Ethyl Cyanoacetate in presence of Ammonia or Amines. II. ICILIO GUARESCHI [and, in part, with ADALBERTO PASQUALI, GALEAZZO PICCININI, GIOVANNI ISSOGLIO, and ENRICO QUENDA] (*Chem. Centr.*, 1905, ii, 681—685; from *Estr. Mem. Reale Accad. Sci. Torino*, ii, 55. Compare *Abstr.*, 1897, i, 168).—When treated with ammonia, β -ketonic esters (1) containing the alkyl group, C_nH_{2n+1} , yield amino-esters, $C_nH_{2n+1} \cdot C(NH_2) : C(C_nH_{2n+1}) \cdot CO_2C_nH_{2n+1}$, and β -ketoamides, $C_nH_{2n+1} \cdot CO \cdot CH(C_nH_{2n+1}) \cdot CO \cdot NH_2$; (2) having an aromatic group attached to the carbonyl, yield amino-amides such as

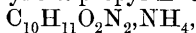


and β -keto-amides such as $CH_2Bz \cdot CO \cdot NH_2$, which are easily formed from the amino-amides (compare *Abstr.*, 1904, i, 891); (3) containing an aromatic alkyl group, such as ethyl benzylacetoacetate, yield the corresponding β -keto-amides, such as $CH_2Ph \cdot CHAc \cdot CO \cdot NH_2$, and small amounts of the amino-esters, as $NH_2 \cdot CMe : C(CH_2Ph) \cdot CO_2Et$; (4) derived from dibasic acids, yield the amino-imides, such as



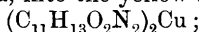
from ethyl acetosuccinate. The β -keto-amides react with ethyl cyanoacetate to form generally dihydroxypyridines.

The *ammonium* compound of cyanomethylpropylglutaconimide (3-cyano-2 : 6-diketo-4-methyl-5-*n*-propyl- Δ^3 -tetrahydropyridine),



obtained by the action of ammonia on ethyl *n*-propylcyanoacetate and ethyl cyanoacetate, crystallises from water, gives a bluish-violet coloration with ferric chloride, a yellow, crystalline precipitate with copper acetate, and a white precipitate with silver nitrate. The free base, $\text{CMe} \begin{smallmatrix} \text{C(CN) \cdot CO} \\ \text{CHPr}^{\alpha} \cdot \text{CO} \end{smallmatrix} \text{NH}$, forms small crystals, melts at 221—222°, gives a violet coloration with alcoholic ferric chloride, and when heated yields γ -cyano- β -methyl- α -propylvinylacetic acid. *n*-Propylacetamidide, $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$, crystallises in long, glistening needles, melts at 105—106°, gives a blue coloration with ferric chloride, and reacts with ammonia and cyanoacetamide in aqueous solution to form cyanomethyl-*n*-propylglutaconimide. Ethyl β -amino- α -*n*-propylcrotonate crystallises in large, glistening leaflets, melts at 44—45°, has a strong odour of peppermint, and becomes yellow on exposure to air. The corresponding *isopropyl* compounds were obtained only in small quantities.

The *ammonium* derivative of cyanomethylisobutylglutaconimide, $\text{CH}_2\text{Pr}^{\beta} \cdot \text{CH} \cdot \text{CMe} : \text{C} \cdot \text{CN}$ or $\text{CH}_2\text{Pr}^{\beta} \cdot \text{CH} \cdot \text{CMe} = \text{C} \cdot \text{CN}$ $\text{NH}_4 \cdot \text{O} \cdot \text{C} : \text{N} \text{---} \text{CO}$ or $\text{CO} \cdot \text{N}(\text{NH}_4) \cdot \text{CO}$, crystallises from water, gives a bluish-violet coloration with ferric chloride, forms white precipitates with silver nitrate and barium chloride, and with cobalt nitrate a rose-coloured precipitate consisting of needles. The yellow precipitate formed with copper sulphate becomes red on addition of more of the reagent, and changes slowly at the ordinary temperature, quickly when warmed, into the yellow anhydrous salt,

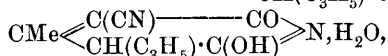


with copper acetate there is formed the salt $\text{Cu} \begin{smallmatrix} \text{CBu}^{\beta} \cdot \text{CMe} : \text{C} \cdot \text{CN} \\ \text{CO} : \text{N} \text{---} \text{CO} \end{smallmatrix}$ or $\text{C}(\text{CN}) : \text{CMe} \cdot \text{CBu}^{\beta} \text{---} \text{Cu} \cdot \text{CBu}^{\beta} \cdot \text{CMe} : \text{C} \cdot \text{CN}$ $\text{CO} \cdot \text{N} = \text{C} \cdot \text{O} \cdot \text{Cu} \cdot \text{O} \cdot \text{C} : \text{N} \text{---} \text{CO}$. The ammonium salt gives

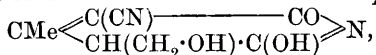
crystalline precipitates also with quinine and cinchonine sulphates and benzylamine and ethylenediamine hydrochlorides. *iso*Butylacetacetamidide, $\text{CH}_2\text{Pr}^{\beta} \cdot \text{CHAc} \cdot \text{CO} \cdot \text{NH}_2$, crystallises in colourless needles, melts at 92°, and gives a violet coloration with ferric chloride. Ethyl aminoisobutylacetacetate, $\text{NH}_2 \cdot \text{CMe} : \text{CBu}^{\beta} \cdot \text{CO}_2\text{Et}$, is crystalline and melts at 42—43°. The *ammonium* derivative of cyanomethyl-*n*-butylglutaconimide forms colourless crystals, gives an intense bluish-violet coloration with ferric chloride, and forms a scarlet precipitate which becomes yellow with copper sulphate, white precipitates with silver nitrate and calcium and barium chloride, a rose-coloured precipitate consisting of rhombohedra or sheaves of needles, a green precipitate with nickel nitrate, and precipitations with quinine and cinchonine sulphates and benzylamine hydrochloride.

n-Butylacetacetamidide, $\text{C}_8\text{H}_{15}\text{O}_2\text{N}$, crystallises in needles, melts at 116—117°, and gives a bluish-violet coloration with ferric chloride. Ethyl amino-*n*-butylacetacetate, $\text{NH}_2 \cdot \text{CMe} : \text{CBu}^{\alpha} \cdot \text{CO}_2\text{Et}$, forms a white, crystalline mass having an odour of peppermint.

The prolonged action of ammonia on ethyl *iso*amylacetoacetate leads to the formation of only a small amount of *ethyl aminoisoamylacetoacetate*, which has an odour of camphor. The *ammonium* derivative of cyanomethylallylglutaconimide gives an intense blue coloration with aqueous ferric chloride. The *copper* derivative is yellow, the *silver* derivative forms a white precipitate, the *barium* derivative crystallises in short prisms. The free base, $\text{CMe} \begin{smallmatrix} \text{C(CN)} \text{---} \text{CO} \\ \text{CH(C}_3\text{H}_5\text{)} \cdot \text{CO} \end{smallmatrix} \text{NH}$ or



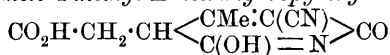
crystallises from water, loses H_2O at $99\text{--}100^\circ$, becomes blue at $100\text{--}110^\circ$, and melts at $172\text{--}173^\circ$. In aqueous solution, the base becomes violet when exposed to the air, forms a crystalline compound with bromine, gives a bluish-green coloration with nitrous acid, and is converted by concentrated sulphuric acid into cyanoallylvinylacetic acid. The action of ethyl hydroxyethylacetoacetate and ammonia on ethyl cyanoacetate leads to the formation of the compound,



which crystallises in colourless or yellow needles, has a slight acid reaction in aqueous solution, gives a violet coloration with ferric chloride or when boiled with bromine water, and forms a *potassium* derivative crystallising in glistening needles. *Benzylacetoacetamide*, $\text{CH}_2\text{Ph} \cdot \text{CHAc} \cdot \text{CO} \cdot \text{NH}_2$, is the principal product of the interaction of ethyl benzylacetoacetate, ethyl cyanoacetate, and ammonia. It crystallises in thick needles, melts at $150\text{--}151^\circ$, gives a violet coloration with alcoholic ferric chloride, and evolves ammonia when boiled with 20 per cent. potassium hydroxide solution.

Cyanobenzylmethylglutaconimide (5-cyano-6-keto-2-hydroxy-3-benzyl-4-methyl-3 : 6-dihydropyridine), $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{O}$, crystallises in short, colourless, glistening prisms, loses H_2O at $100\text{--}110^\circ$, becomes brown at 215° , melts at $217\text{--}218^\circ$, gives a bluish-violet coloration with alcoholic ferric chloride, and when boiled with 60 per cent. sulphuric acid yields cyanobenzylmethylvinylacetic acid. The *ammonium*, $\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2 \cdot \text{NH}_4$, *barium*, *calcium*, *magnesium* ($9\text{H}_2\text{O}$), *silver*, *copper*, *quinine*, *cinchonine*, and *strychnine* derivatives are described.

5-Cyano-2 : 6-diketo-4-methyl- Δ^4 -tetrahydropyridyl-3-acetic acid,



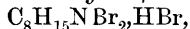
or $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe} \cdot \text{C(CN)} \\ \text{CO} \text{---} \text{NH} \end{smallmatrix} \text{CO}$, crystallises in colourless needles, melts at 202° , and gives an intense blue coloration when warmed with 5 per cent. potassium nitrite solution, a red coloration with bromine water, and a dark violet precipitate with ferric chloride. The *di-ammonium*, $\text{C}_7\text{H}_4\text{ON}_2(\text{ONH}_4) \cdot \text{CH}_2 \cdot \text{CO}_2\text{NH}_4$, *mono-ammonium*, $\text{C}_7\text{H}_5\text{O}_2\text{N}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{NH}_4$, *barium*, $\text{C}_9\text{H}_6\text{O}_4\text{N}_2\text{Ba} \cdot 2\text{H}_2\text{O}$, *silver*, $\text{C}_9\text{H}_7\text{O}_4\text{N}_2\text{Ag} \cdot \text{H}_2\text{O}$, and *di-silver*, $\text{C}_9\text{H}_6\text{O}_4\text{N}_2\text{Ag}_2$, salts are described.

β -Aminocinnamamide, $\text{NH}_2 \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH}_2$, crystallises from water in glistening leaflets, melts at $164\cdot5\text{--}165^\circ$, and gives a rose coloration with nitrous fumes in sulphuric acid solution, and a rose-violet

with alcoholic or aqueous ferric chloride. *Cyanophenylglutaconimide*, $C_{18}H_8O_2N_2 \cdot H_2O$, crystallises in needles, loses H_2O at $100-110^\circ$, becomes brown at $265-270^\circ$, and melts at about 285° . It gives a green coloration with potassium nitrite and sulphuric acid and a red with bromine water, and when treated with 60 per cent. sulphuric acid is converted into γ -cyano- β -phenylvinylacetic acid. The *ammonium*, *magnesium*, *barium* ($5H_2O$), and *copper* salts are described.

G. Y.

Reduction of 4-Methyl-3-ethylpyridine with Sodium and Alcohol. WILHELM KOENIGS and KARL BERNHART (*Ber.*, 1905, 38, 3042—3049).— β -Collidine or 4-methyl-3-ethylpyridine (Koenigs, *Abstr.*, 1894, i, 477), when reduced with excess of sodium and absolute ethyl alcohol, yields a mixture of a tetrahydro- and a hexahydro-derivative, which are best separated by conversion of the tetrahydro-derivative into *dibromohexahydro- β -collidine hydrobromide*,



which is insoluble in cold ethyl acetate, whereas hexahydro- β -collidine hydrobromide is readily soluble. The hydrobromide crystallises in slender needles, melts and decomposes at $163-164^\circ$, and is optically inactive. The dibromo-derivative itself has been obtained only as a resin with an odour of camphor. With nitrous acid, the hydrobromide yields a *nitroso*-derivative melting at $107-108^\circ$. Tetrahydro- β -collidine, obtained by the action of zinc dust and sulphuric acid on the hydrobromide, distils at 177° under 719 mm. pressure, and yields an *acid tartrate* melting at $165-167^\circ$. From this a normal *oxalate*, $C_{18}H_{32}O_4N_2$, melting and decomposing at 199° , has been prepared; it is optically inactive. The *carbonate* melts at $60-62^\circ$. The *aurichloride*, $C_8H_{15}N \cdot HAuCl_4$, crystallises in yellow plates, melts at $148-149^\circ$, and is sensitive to light. The *platinichloride* melts and decomposes at 194° and the *picrate* melts at $127-128^\circ$. The pure base immediately decolorises permanganate.

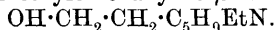
Hexahydro- β -collidine hydrogen tartrate crystallises in colourless needles and melts and decomposes at $194-195^\circ$. The normal *oxalate* melts at $185-187^\circ$. The hydrochloride dissolves readily in water, the *aurichloride* crystallises from a mixture of alcohol and ether in yellow needles melting at $126-128^\circ$. The *platinichloride* melts and decomposes at 208° . The base does not decolorise acidified permanganate, and with a chloroform solution of bromine yields a perbromide.

J. J. S.

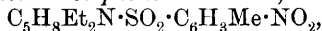
3:4-Diethylpyridine, 3:4-Diethylpiperidine, and 3-Ethylquinuclidine. WILHELM KOENIGS and KARL BERNHART (*Ber.*, 1905, 38, 3049—3057. Compare *Abstr.*, 1904, i, 925).—3:4-Diethylpyridine is obtained when 3-ethylpyridyl-4-ethanol (*Abstr.*, 1902, i, 395) is reduced with hydriodic acid and red phosphorus and, after removal of the phosphorus, treated with zinc dust in a freezing mixture and kept overnight. The base, after purification by means of the picrate, distils at $207-209^\circ$ under 710 mm. pressure. The *aurichloride*, $C_9H_{13}N \cdot HAuCl_4$, crystallises from dilute hydrochloric acid in slender, yellow needles and melts at $111-112^\circ$. The *platinichloride* crystal-

lises in orange-red plates, melting and decomposing at 221° . The *mercurichloride* forms colourless needles melting at $90-98^{\circ}$. The *picrate* forms slender needles sparingly soluble in water and melts at 139° .

When reduced with sodium and alcohol, part of the base is transformed into 3:4-diethylpiperidine, but unaltered base and its tetrahydro-derivative are also present. 3:4-Diethylpiperidine is most readily obtained from methylolhexahydro- β collidine,



The aurichloride of this melts at $124-126^{\circ}$. When the free base is reduced with hydriodic acid and red phosphorus, it yields the *hydriodide*, $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{C}_5\text{H}_9\text{EtN}\cdot\text{HI}$. This crystallises from ice-cold water, melts at 96° , is readily soluble and, on reduction with zinc dust and hydriodic acid at low temperatures, yields 3:4-diethylpiperidine. The base distils at 193° under 720 mm. pressure, the *hydrochloride* crystallises from ethyl acetate in colourless needles melting at $107-108^{\circ}$. The *platinichloride* melts at $159-160^{\circ}$, the *aurichloride* at $120-130^{\circ}$, the *hydrobromide* at $102-103^{\circ}$, and the *picrate* at $107-108^{\circ}$. The *phenyl-carbimide* derivative crystallises from light petroleum and melts at $87-88^{\circ}$; the *p-nitrotoluenesulphone* derivative,



crystallises from alcohol and melts at $89-90^{\circ}$. The corresponding derivative of piperidine melts at 85° .

The hydriodide, melting at 96° , yields β -ethylquinuclidine, identical in all respects with the compound already described (Abstr., 1904, i, 925). Its properties are those of a tertiary base, and the methiodide melts at 130° and shows all the properties of a quaternary ammonium iodide. The base is extremely stable, is not decomposed by dilute hydrochloric acid at $170-180^{\circ}$, by phosphoric acid at $190-200^{\circ}$, by fuming hydrobromic acid at $190-200^{\circ}$, or by alcoholic potash. It appears to combine with bromine, yielding a colourless additive compound melting at 152° , and this with sulphurous acid yields the unaltered base.

J. J. S.

2-Methyl-6-pyrophthalone. A. SCHOLZE (*Ber.*, 1905, 38, 2806—2809. Compare Huber, Abstr., 1903, i, 576; Gaebelé, *ibid.*, 1904, i, 88).—2-Methyl-6-pyrophthalone, $\text{C}_5\text{NH}_3\text{Me}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{C}_6\text{H}_4 \end{smallmatrix}\text{CO}$,

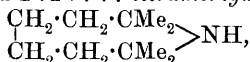
is obtained when phthalic anhydride, 2:6-dimethylpyridine (Ahrens, this vol., i, 232), and a fragment of zinc chloride are heated for eight hours at 170° . It crystallises from alcohol, by spontaneous evaporation, in deep bluish-red needles melting at $210-211^{\circ}$, is soluble in most organic solvents and in concentrated hydrochloric acid. Most of the salts dissolve readily in alcohol, chloroform, or acetic acid, and melt at about 210° owing to dissociation. The following have been prepared: *hydrochloride*, $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}\cdot\text{HCl}$, *hydrobromide*, *platinichloride*, *mercurichloride*, and *sodium salt*, $\text{C}_5\text{NH}_3\text{Me}\cdot\text{CNa}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \text{C}_6\text{H}_4 \end{smallmatrix}\text{CO}$.

It has not been found possible to condense the pyrophthalone with a further quantity of phthalic anhydride.

J. J. S.

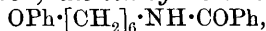
Preparation of New Polymethyleneimines by Ladenburg's Method. MICHAEL I. KONOWALOFF and S. WOINITSCH-SIANOSCHENSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 523—530).—On subjecting small quantities of *s*-tetramethyltetramethylenediamine ($\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$) hydrochloride to dry distillation and collecting the distillate in hydrochloric acid, an oily mixture of the hydrocarbons, C_8H_{16} and C_8H_{14} , having the boiling point 130 — 135° at 754 mm. pressure and a sp. gr. 0.772 at 0° and 0.759 at 17.5° , is obtained, together with a mixture of bases from which was isolated the *benzoyl* derivative, $\text{C}_8\text{H}_{16}\text{NBz}$, melting at 67.5 — 68° , of 2 : 2 : 5 : 5-tetramethylpyrrolidine (2 : 2 : 5 : 5-tetramethyltetramethyleneimine), $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CMe}_2 \end{array} > \text{NH}$.

Similarly, dry distillation of *s*-tetramethylhexamethylenediamine ($\text{NH}_2 \cdot \text{CMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{CMe}_2 \cdot \text{NH}_2$) hydrochloride yields : (1) a mixture of unsaturated hydrocarbons, $\text{C}_{10}\text{H}_{20}$ and $\text{C}_{10}\text{H}_{18}$; (2) a mixture of bases from which was isolated 2 : 2 : 7 : 7-tetramethylhexamethyleneimine,



which forms a very stable hydrate, $\text{C}_{10}\text{H}_{21}\text{N} \cdot \text{H}_2\text{O}$, melting at 36 — 36.5° , boiling at 236.5 — 237° under 749 mm. pressure, and having a sp. gr. 0.87913 at $16/0^\circ$ and $n_D^{20} 1.45782$ at 16° ; the anhydrous base (?) melts at 140.5 — 141° and readily combines with water; the *benzoyl* derivative, $\text{C}_{10}\text{H}_{20}\text{NBz} \cdot \text{H}_2\text{O}$, crystallises from light petroleum in silky needles melting at 76.5 — 77° , and dissolves readily in alcohol or benzene. The following salts of 2 : 2 : 7 : 7-tetramethylhexamethyleneimine were prepared: the *oxalate*, melting at 226° ; the *hydrobromide*, melting at 149° ; the *sulphate*, *nitrate*, and *aureibromide*; the *picrate*, melting at 117.5 — 118° . T. H. P.

Synthesis of Hexamethyleneimine—the Cyclic Homologue of Piperidine. JULIUS VON BRAUN and ADOLF STEINDORFF (*Ber.*, 1905, **38**, 3083—3094).— ζ -Phenoxyhexylamine, $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{NH}_2$, is obtained by the reduction of the nitrile of phenoxyhexoic acid (this vol., i, 207, 342) with sodium and alcohol. It can be isolated by means of its sparingly soluble *hydrochloride*, which crystallises from its aqueous solution in compact prisms melting at 140° . The base is a colourless oil distilling at 167 — 169° ; it has a faint basic odour and solidifies when cooled with ice. The *platinichloride* forms yellowish-red crystals from water, turns black at 191° , and is molten at 199° . The *picrate* melts at 135° ; the *benzoyl* derivative,

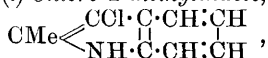


crystallises from dilute alcohol and melts at 80° , and the *benzenesulphonyl* derivative, $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{NH} \cdot \text{SO}_2\text{Ph}$, melts at 57 — 58° . In the presence of alkali hydroxide, the base readily absorbs carbon dioxide, yielding the sparingly soluble *sodium phenoxyhexylcarbamate*, $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{NH} \cdot \text{CO}_2\text{Na}$, which crystallises in glistening plates. It melts at 80° , at the same time evolving carbon dioxide and leaving a wax-like residue of the *sodio-amide*, $\text{OPh} \cdot [\text{CH}_2]_6 \cdot \text{NHNa}$, which is decomposed by water into phenoxyhexylamine and sodium hydroxide.

ζ -Chlorohexylamine (this vol., i, 635) is formed when the phenoxy-compound is heated with four times its weight of concentrated hydrochloric acid at 90° . The corresponding ζ -bromohexylamine is prepared by heating the phenoxy-derivative at 80° with hydrobromic acid saturated at 0° . The *hydrobromide* is hygroscopic, and the *picrate* melts at 127° and dissolves sparingly in water. The chloro- and bromo-bases are stable at low temperatures, but when heated alone or in presence of water they yield *hexamethyleneimine* salts and their polymerides. For the preparation of hexamethyleneimine, it is not necessary to use the pure base; the product of decomposition of the phenoxy-compound with hydrobromic acid is freed from phenol, made alkaline, and distilled in steam. The yield of base is some 10 per cent. It is a mobile liquid, miscible with water, has an odour like piperidine, and distils at about 120 — 130° . The *hydrochloride* has been obtained in the form of a syrup only; the *platinichloride* crystallises in reddish-yellow needles, melting and decomposing at 148 — 149° . The *aureichloride* and *picrate* are obtained as red oils which slowly solidify. The *benzenesulphonyl* derivative is an oil and is insoluble in water. When completely methylated, the base yields the *quaternary ammonium iodide*, $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \end{matrix} > \text{NMe}_2\text{I}$, which melts at 214 — 215° . The corresponding *platinichloride* melts between 245° and 255° .

The polymeric base, $(\text{C}_6\text{NH}_{13})_n$, is not volatile with steam, and forms a wax-like mass insoluble in water or ether, but soluble in chloroform or alcohol or acids. Most of the salts and derivatives are oily or pasty. The *platinichloride* is insoluble in cold water, and turns black and melts at 228° . When completely methylated, it yields a *quaternary* salt, the *platinichloride* of which dissolves extremely sparingly in water and decomposes at 255° .
J. J. S.

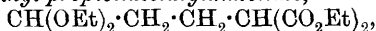
Action of Sulphuryl Chloride on 2-Methylindole (Methylketole). GIROLAMO MAZZARA and ALESSANDRO BORGIO (*Gazzetta*, 1905, 35, ii, 100—104).—3-(*l*)-Chloro-2-methylindole,



prepared by the action of sulphuryl chloride (1 mol.) on an absolute ethereal solution of 2-methylindole (1 mol.), crystallises from light petroleum in large, shining, nacreous scales melting at 98° , and is soluble in dilute sulphuric acid, to which it imparts a feeble amethyst coloration; readily soluble in ether, and slightly so in water. It has a faecal odour resembling that of 3-methylindole, and a pine splinter moistened with hydrochloric acid and immersed in its vapour turns red, whilst paper on which it is placed becomes first yellow and later red. When inhaled, the vapour produces nausea and dizziness.

T. H. P.

Constitution of the Indole Group in Albumin. II. Synthesis of Indole-3-propionic Acid (Nencki's Scatoleacetic Acid). ALEXANDER ELLINGER (*Ber.*, 1905, 38, 2884—2888. Compare Abstr., 1904, i, 639).—*Ethyl propionacetylmalonate*,



is formed by heating β -chloropropionacetal with ethyl malonate and sodium ethoxide in alcoholic solution in a closed vessel at 130—140° for four hours. It is a colourless liquid which boils at 170° under 20 mm. pressure, and when heated with water at 180—190° under pressure is converted into γ -aldehydobutyric acid, $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$; on evaporation of its solution, this is obtained as a colourless syrup which is slightly volatile in a current of steam. This was converted into the *phenylhydrazone*, boiled with 10 per cent. alcoholic sulphuric acid, and poured into water; the viscid, brown oil so obtained, on hydrolysis with alcoholic potassium hydroxide, yielded *indole-3-propionic acid*, $\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{CH}=\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which, after purification by conversion into its mercuric salt, was found to be identical with Nencki's scatoleacetic acid melting at 134°.

Indole-3-methylacetic acid, $\text{NH}\langle\text{C}_6\text{H}_4\rangle\text{CH}=\text{C}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, prepared in the same manner from aldehydoisobutyric acid (Perkin and Sprankling, *Trans.*, 1889, 75, 11), separates from water as an oil which solidifies in the cold to a mass of thick prisms, melts at 107° in aqueous solution, has an odour of scatole, and with potassium nitrite in acetic acid solution forms an oily *product* which gradually resinifies. G. Y.

Thalleioquinine Reaction of Quinine and Jaffé's Kynurenic Acid Reaction. HERMANN FÜHNER (*Ber.*, 1905, 38, 2713—2715).—Since not only quinine, but also cupreine, gives the thalleioquinine reaction, it appeared likely that *p*-hydroxyquinoline itself would give the reaction. The author finds that this is the case.

5:5-Dichloro-6-ketoquinoline, prepared by passing chlorine into an ice-cold solution of *p*-hydroxyquinoline hydrochloride, separates from light petroleum in prisms and melts at 58°; its *hydrochloride* melts and decomposes at 240°. The solutions of base and hydrochloride respectively in sodium carbonate and in alkali hydroxides are brown, whilst their ammoniacal solutions are green or blue.

When γ -hydroxyquinoline is evaporated to dryness with potassium chlorate and hydrochloric acid and ammonia added to the residue, a brown coloration is at first produced, and this becomes brown and then green. Jaffé's kynurenic acid reaction is accordingly applicable to γ -hydroxyquinoline. The colour-changes when *p*-hydroxyquinoline is used are similar, except that the brown coloration is not so intense, whilst with *o*-hydroxyquinoline the green coloration is very transient and the brown coloration is stable. A. McK.

Quinoline Derivatives. I. 5-Quinaldine Derivatives. HERMAN DECKER and PERCY REMFRY (*Ber.*, 1905, 38, 2773—2777. Compare E. Alber, this vol., i, 235; Doebner and Miller, *Abstr.*, 1884, 1373; Gerdeissen, *ibid.*, 1889, 520; Marckwald, *ibid.*, 1893, i, 727).—The following generalisation is stated. On nitrating quinoline and its derivatives, the nitro-group is substituted simultaneously in the positions 5 and 8 of the benzene ring, provided no strongly positive or negative groups are present. In quinoline itself, the proportions of the two

nitro-products formed are roughly equal, but when neutral substituents such as methyl or halogen are present, one isomeride preponderates. The two products obtained on nitrating 2-methylquinoline should thus be the 5- and 8-nitro-derivatives, and the compound stated to be 7-nitro-2-methylquinoline by Doebner and Miller is shown to be the 5-nitro-2-methylquinoline.

5-Nitro-2-methylquinoline methiodide, $C_9H_{11}O_2N_2I$, obtained by the action of methyl sulphate and the subsequent addition of solid potassium iodide, forms orange-yellow crystals and melts at 201° . The *picrate*, $C_{17}H_{13}O_9N_5$, crystallises in yellow needles and melts at 151.5° . 5-Nitro-2-methylquinolone (Abstr., 1892, 879) is obtained when the methiodide is oxidised in alkaline solution with potassium ferricyanide, and thus the position of the nitro-group is established.

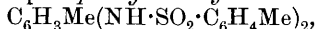
The following compounds are 5- and not 7-substituted derivatives. Cyanomethylquinoline (Rist, Abstr., 1891, 329), quinaldinesulphonic acid, β -hydroxymethylquinoline (Doebner and Miller, Abstr., 1884, 1373); the methylquinolinecarboxylic acid melting at 285° ; the so-called *m*-methylquinaldine (Abstr., 1894, i, 184); methylquinoline-acrylic acid (Abstr., 1886, 265), methylquinolinealdehyde (Abstr., 1889, 522), and Claus and Momberger's nitro- and amino-quinaldinecarboxylic acids (Abstr., 1898, i, 206).

In both quinoline and quinaldine syntheses, the chief product is a 5-substituted derivative (compare Rist). J. J. S.

Action of 5-Methylacridine on Benzaldehyde and *m*-Nitrobenzaldehyde. KONRAD FRIEDLÄNDER (*Ber.*, 1905, 38, 2840—2842).—*Acridylphenylethanol*, $C_{13}H_8N \cdot CH_2 \cdot CHPh \cdot OH$, formed by heating 5-methylacridine and benzaldehyde together in a sealed tube at 100° , crystallises in yellow needles, melts at 196 — 198° , does not form an additive compound with bromine, and does not distil in a current of steam. The *platinichloride*, $(C_{21}H_{17}ON)_2 \cdot H_2PtCl_6$, forms a yellow powder; the *mercurichloride*, $(C_{21}H_{17}ON)_2 \cdot H_2HgCl_4$, forms a yellow, sparingly soluble powder which melts at 212 — 215° .

m-Nitrocinnamethylacridine, $C_{13}H_8N \cdot CH \cdot CH \cdot C_6H_4 \cdot NO_2$, formed when 5-methylacridine is heated with *m*-nitrobenzaldehyde in a sealed tube at 100° , separates from alcohol as a yellow, crystalline powder, melts at 206 — 208° , and has an aromatic odour. The *hydrochloride*, $C_{21}H_{14}O_2N_2 \cdot HCl$, sulphate, $(C_{21}H_{14}O_2N_2)_2 \cdot H_2SO_4$, and *aureichloride*, $C_{21}H_{14}O_2N_2 \cdot HAuCl_4$, are described. The *dibromide*, $C_{21}H_{14}O_2N_2Br_2$, forms a red, crystalline powder, which becomes colourless at 200° and is not melted at 300° . G. Y.

[*Bistoluene-p*-sulphonyl-*m*-tolylenediamide.] K. OEHLER (D.R.-P. 158662).—*Bistoluene-p*-sulphonyl-*m*-tolylenediamide,



prepared by boiling together 1:2:4-tolylenediamine and toluene-*p*-sulphonic chloride in alcoholic solution (compare Reverdin and Crépieux, Abstr., 1902, i, 238), melts at 192 — 193° and closely resembles the corresponding phenylene derivative. When fused with sulphur at 240 — 260° in presence of an aromatic amine of high boiling point, such as benzidine or naphthylamine, yellow dyes are obtained.

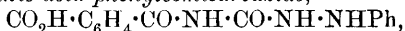
C. H. D.

Reduction of Hydrazones in Acid Solution. HARTWIG FRANZEN (*J. pr. Chem.*, 1905, [ii], 72, 211—219).—When reduced with zinc dust in alcoholic acetic acid solution, phenylbenzylidenehydrazine yields aniline, benzyaniline, ammonia, benzylamine, and dibenzylamine. The reaction is explained by the following series of equations: (1) $\text{NHPh}\cdot\text{N}:\text{CHPh} + \text{H}_2 = \text{NHPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$; (2) $\text{NHPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph} + \text{H}_2 = \text{NH}_2\text{Ph} + \text{CH}_2\text{Ph}\cdot\text{NH}_2$; (3) $\text{NHPh}\cdot\text{N}:\text{CHPh} + \text{H}_2\text{O} = \text{NHPh}\cdot\text{NH}_2 + \text{C}_6\text{H}_5\cdot\text{COH}$; (4) $\text{NHPh}\cdot\text{NH}_2 + \text{H}_2 = \text{NH}_2\text{Ph} + \text{NH}_3$; (5) $\text{NH}_2\text{Ph} + \text{C}_6\text{H}_5\cdot\text{COH} = \text{NPh}\cdot\text{CHPh} + \text{H}_2\text{O}$; (6) $\text{NPh}\cdot\text{CHPh} + \text{H}_2 = \text{NHPh}\cdot\text{CH}_2\text{Ph}$; (7) $\text{CH}_2\text{Ph}\cdot\text{NH}_2 + \text{C}_6\text{H}_5\cdot\text{COH} = \text{CH}_2\text{Ph}\cdot\text{N}:\text{CHPh} + \text{H}_2\text{O}$; (8) $\text{CH}_2\text{Ph}\cdot\text{N}:\text{CHPh} + \text{H}_2 = \text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$.

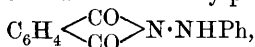
On reduction in the same manner, phenyl-*p*-isopropylbenzylidenehydrazine yields ammonia, aniline, *p*-isopropylphenylbenzylamine, *p*-isopropylbenzylamine, and di-*p*-isopropylbenzylamine; phenyl-*o*-hydroxybenzylidenehydrazine yields *o*-hydroxybenzyaniline; diphenylbenzylidenehydrazine yields diphenylamine, benzylamine, and dibenzylamine; benzylideneaniline yields benzyaniline, and benzylidenebenzylamine yields dibenzylamine.

Benzylamine remains unchanged when boiled in alcoholic acetic acid solution in a reflux apparatus for nine hours. No dibenzylamine was formed on boiling benzylamine with zinc acetate in alcoholic acetic acid solution or on treatment of benzylamine with zinc dust in glacial acetic acid solution. G. Y.

Action of Phenylsemicarbazide and Semicarbazide Hydrochloride on Phthalic Anhydride. FREDERICK L. DUNLAP (*J. Amer. Chem. Soc.*, 1905, 27, 1091—1107).—When molecular proportions of phenylsemicarbazide and phthalic anhydride are heated together at 140—145°, *phthalic acid phenylsemicarbazide*,

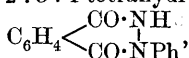


is produced, which crystallises from glacial acetic acid in small clusters of white, microscopic needles, melts and decomposes at 191—192°, and is slightly soluble in alcohol or water. If this substance is heated for half an hour at 180—185°, it undergoes decomposition with formation of carbon dioxide, ammonia, phenylhydrazine, phthalimide, phthalylphenylhydrazine (anilinophthalimide), and 1:4-diketo-2-phenyl-1:2:3:4-tetrahydrophthalazine. Phthalylphenylhydrazine,



described by Hötte (Abstr., 1886, 353) and Pickel (Abstr., 1886, 545), crystallises in two forms, a stable yellow form and a labile white form, both melting at 179—179.5°. The stable modification can be obtained free from the labile form by crystallisation from hot glacial acetic acid, whilst the labile form is best prepared by crystallisation from alcohol. The yellow modification forms holohedral, monoclinic crystals [$a:b:c = 1.1671:1:0.7848$; $\beta = 54^\circ 50'$], whilst the white modification crystallises in holohedral, rhombic prisms [$a:b:c = 0.2526:1:0.9118$].

1:4-Diketo-2-phenyl-1:2:3:4-tetrahydrophthalazine,



which was first described by Pellizzari (Abstr., 1886, 1025) under the

name of phthalylphenylhydrazide, and afterwards by Hötte (Abstr., 1887, 669), who termed it β -phthalylphenylhydrazine, crystallises in white needles and melts at 210° .

When molecular proportions of phthalimide and phenylhydrazine are heated together at 120° , anilinophthalaldiamide (Hötte, *loc. cit.*) is produced, which is decomposed by heat with formation of ammonia, phthalylphenylhydrazine, and 1:4-diketo-2-phenyl-1:2:3:4-tetrahydrophthalazine.

If a solution of phthalic anhydride (1 mol.) and phenylhydrazine (1 mol.) in chloroform is left for several hours, anilinophthalamic acid separates, which is decomposed by heat with production of phthalylphenylhydrazine and 1:4-diketo-2-phenyl-1:2:3:4-tetrahydrophthalazine, the relative proportions of these substances formed depending on the temperature.

Phthalylsemicarbazide, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot CO \cdot NH \cdot NH_2$, obtained by heating a mixture of semicarbazide hydrochloride and phthalic anhydride at 160° , crystallises in white needles, melts and decomposes at 262° , and is slightly soluble in boiling water or alcohol. This compound is readily soluble in dilute alkali and, on acidifying the solution, *phthalic acid semicarbazide*, $CO_2H \cdot C_6H_4 \cdot CO \cdot NH \cdot CO \cdot NH \cdot NH_2$, is precipitated, which crystallises in slender, white prisms, is soluble in alcohol or glacial acetic acid, and, when heated, is converted into phthalylsemicarbazide and then melts at 262° . E. G.

Oxazones. ROBERT GNEHM and LEO BAUER (*J. pr. Chem.*, 1905, [ii], 72, 249—277).—*Diethylaminoazobenzene*, $NEt_2 \cdot C_6H_4 \cdot N_2Ph$, formed by the action of phenyldiazonium nitrate on diethylaniline in aqueous sodium acetate solution, crystallises in golden leaflets or brownish-orange needles, melts at 97.8° , and dissolves in dilute acids to form red solutions. The *hydrochloride*, $C_{16}H_{20}N_3Cl$, crystallises from alcohol in flat, orange needles, forms carmine solutions, and is hydrolytically dissociated in aqueous solution; the *sulphate*, $C_{16}H_{19}N_3 \cdot H_2SO_4$, crystallises in red leaflets or slender needles, melts at 137° , forms blood-red solutions, and yields the free base when boiled with water.

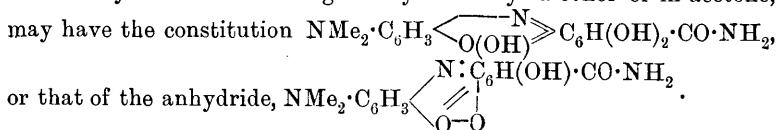
p-Tolueneazodiethylaniline, $NEt_2 \cdot C_6H_4 \cdot N_2 \cdot C_7H_7$, formed by the action of diazotised *p*-toluidine on diethylaniline, crystallises from ether or alcohol in orange leaflets and melts at 113° . The *hydrochloride*, $C_{17}H_{21}N_3 \cdot HCl$, forms thin, orange plates and melts at 179° ; the *sulphate*, $C_{17}H_{21}N_3 \cdot H_2SO_4$, crystallises in red needles and melts at 179° .

α -Naphthaleneazodiethylaniline, $NEt_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_7$, crystallises in glistening, green leaflets and melts at 108° . The *hydrochloride* forms a brown, viscous resin; the *sulphate*, $C_{20}H_{21}N_3 \cdot H_2SO_4$, crystallises from alcohol in brown leaflets and melts at 189.5° .

β -Naphthaleneazodiethylaniline, formed from β -naphthylamine and diethylaniline, crystallises from light petroleum or nitrobenzene in brownish-red needles or leaflets and melts at 137.6° . The *hydrochloride*, $C_{20}H_{21}N_3 \cdot HCl$, crystallises in golden-brown leaflets and melts at 174° ; the *sulphate* forms golden-brown leaflets and melts at 171° .

The yield of gallamine-blue, $C_{15}H_{13}O_4N_3 \cdot HCl$, obtained by treating gallamide in alcoholic solution with nitrosodimethylaniline, is largely

increased by using an excess of the latter, part of which undergoes reduction during the reaction. The dye forms dark green, glistening, microscopic plates, which appear blue by transmitted light, decomposes above 320° , and is easily soluble in boiling nitrobenzene or glacial acetic acid, less so in boiling water, or amyl, ethyl, or methyl alcohol, and only sparingly so in benzene, xylene, chloroform, or acetone; the solutions are violet-blue to blue, and on addition of alkali hydroxides deposit the base as a bluish-violet, flocculent precipitate. The base, which forms a blue, metallic powder, melts at 251° , and is moderately soluble in boiling methyl or ethyl alcohol or in acetone, may have the constitution

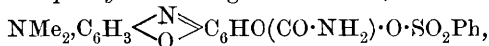


Cœlestine-blue (*p*-diethylaminodihydroxycarbamidophenoxazonium chloride) is formed from nitrosodiethylaniline and gallamide in the same manner as gallamine-blue, but is more soluble. The *dye-base*, $\text{C}_{17}\text{H}_{17}\text{O}_4\text{N}_3$ or $\text{C}_{17}\text{H}_{19}\text{O}_5\text{N}_3$, resembles that of gallamine-blue. Diethylaminoazobenzene and gallamide condense in glacial acetic acid solution at 110 – 120° . The *dye-base*, which has the constitution of the base of cœlestine-blue, separates from the alkaline solution as a blue, flocculent precipitate, crystallises from benzene in microscopic leaflets, and melts under boiling water.

The leuco-derivatives of the gallocyanin dyes are obtained as the stannous chloride or the zinc chloride double salt by reduction with stannous chloride or zinc and hydrochloric acid. These leuco-derivatives are unstable with the exception of the derivatives of prune.

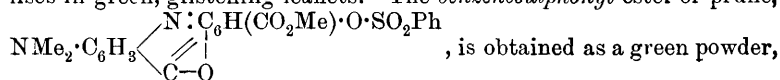
Leuco-prune hydrochloride is formed best by the action of concentrated hydrochloric acid on leuco-diacetylprune. Leuco-prune zinc chloride, $\text{C}_{16}\text{H}_{16}\text{O}_5\text{N}_2\text{Cl} \cdot \text{ZnCl}_2$, crystallises from glacial acetic acid in greenish-yellow needles, melts and decomposes at 268° , dissolves in water to form a solution which changes through brown to violet-red, and finally to violet-blue, and in concentrated hydrochloric acid forms a brown, or in concentrated sulphuric acid a violet, solution, which on dilution with water becomes red.

The *benzenesulphonyl* ester of gallamine-blue,



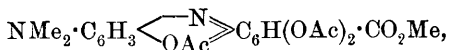
formed by the action of benzenesulphonyl chloride on the dye dissolved in aqueous sodium carbonate, crystallises from aniline in long, glistening needles, or from a mixture of nitrobenzene, alcohol, and ether in glistening, green, microscopic leaflets, decomposes at 230 – 240° , and is moderately soluble in boiling acetone, xylene, or methyl, ethyl, or amyl alcohol, forming solutions which are violet-blue by transmitted, carmine-red by reflected, light.

The *benzenesulphonyl* ester of cœlestine-blue, $\text{C}_{23}\text{H}_{21}\text{O}_6\text{N}_3\text{S}$, crystallises in green, glistening leaflets. The *benzenesulphonyl* ester of prune,



which forms in boiling aqueous sodium hydroxide a brown, in hydrochloric acid a red, and in sulphuric acid a bluish-violet, solution. The *o*-toluenesulphonyl ester of prune, $C_{23}H_{20}O_7N_2S$, crystallises from hot nitrobenzene in dark green, glistening leaflets. The *p*-toluenesulphonyl ester of prune crystallises in flat, green, microscopic needles, and when boiled with acetic anhydride in a reflux apparatus yields the *diacetyl* derivative, $C_{27}H_{26}O_9N_2S$, which crystallises in yellow needles, melts at 245° , and dissolves in concentrated sulphuric acid to form a bluish-green solution.

When heated with sodium acetate, acetic anhydride, and glacial acetic acid at 100° , and finally at 150° , prune forms a *triacetyl* derivative, $NMe_2 \cdot C_6H_3 \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} \text{Ac} \text{C}_6H(OAc)_2 \cdot CO_2Me$, or

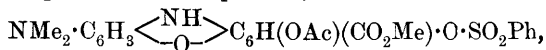


or $NMe_2 \cdot C_6H_4 \cdot NH \cdot C_6H(OAc)_3 \cdot CO_2Me$, which crystallises in lemon-yellow needles, sinters at 219° , and melts at 225° . It dissolves in concentrated sulphuric acid to form an emerald-green or blue solution, which becomes red on addition of water, and when treated with ammonia deposits the leuco-base as an apple-green, flocculent precipitate (compare Nietzki and Otto, Abstr., 1888, 949; Möhlau and Klimmer, *Zeit. Farb. Textilchem.*, 1902, i, 65; Henrich and Schierenberg, Abstr., 1904, i, 1049).

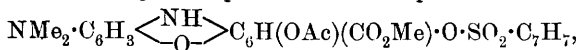
When boiled with acetic anhydride in a reflux apparatus, the *o*-toluenesulphonyl ester of prune forms a *diacetyl* derivative, $C_{27}H_{25}O_9N_2S$, which crystallises from ethyl acetate in yellowish-green needles and melts at $201\text{--}202^\circ$. The *product* obtained on boiling the benzenesulphonyl ester of prune with acetic anhydride and sodium acetate crystallises from ethyl acetate in small, yellow needles, sinters at 116° , and melts at 121° .

When reduced with stannous chloride and acetic anhydride in presence of sodium acetate, prune forms *diacetyl-leuco-prune*, $C_{20}H_{20}O_7N_2$, which is formed also by heating leuco-prune with acetic anhydride and sodium acetate at 130° in an atmosphere of carbon dioxide. It crystallises from toluene in orange needles, or from alcohol in long, golden needles, and melts at 168° . When heated with acetic anhydride, stannous chloride, and sodium acetate at 130° , leuco-prune forms a *mixture* of di- and tri-acetyl derivatives, which crystallises in yellow needles and melts at 184.5° .

Acetyl-leuco-prune benzenesulphonate,



is formed by shaking the benzenesulphonate with acetic anhydride and stannous chloride and boiling the product with sodium acetate. It crystallises in yellow needles, melts at 146° , and dissolves in concentrated sulphuric acid, forming a blue solution which becomes red on dilution. *Acetyl-leuco-prune o-toluenesulphonate*,



formed in the same manner as the acetylbenzenesulphonate, crystal-

lises in orange needles, which appear violet-blue by transmitted light, and melts at 211°.

Acetyl-leuco-prune p-toluenesulphonate crystallises from alcohol in short, yellow needles and melts at about 169°. Leuco-prune hydrochloride is obtained on hydrolysis of the diacetyl, but not of the triacetyl, derivative with hydrochloric acid. G. Y.

Piperazine Derivatives from Methylchloroethylamine and Chloroethylpiperidine. LUDWIG KNORR, H. HÖRLEIN, and PAUL ROTH (*Ber.*, 1905, 38, 3136—3141. Compare this vol., i, 1; Knorr, *Abstr.*, 1904, i, 938; Marckwald and Frobenius, *Abstr.*, 1902, i, 22).—Marckwald and Frobenius' polymeric base, $C_6H_{14}N_2$, formed along with *n*-methyleneethylenimine by the action of sodium hydroxide on methylchloroethylamine hydrochloride, is shown to be 1:4-dimethylpiperazine. It boils at 131—132° under 750 mm. pressure; the picrate decomposes at 280°; the aurichloride decomposes at 220°; the platinichloride decomposes at 270°.

Marckwald and Frobenius' supposed ethylenepiperidinium chloride, obtained by boiling 1-chloroethylpiperidine, is diethylenedipiperidinium chloride, $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix} NCl \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix} NCl \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \\ \diagdown CH_2 \cdot CH_2 \end{smallmatrix} CH_2$. The picrate, $C_{26}H_{32}O_{14}N_8$, crystallises from boiling water in glistening, rhombic, dichroic leaflets and decomposes at about 300°. When distilled with 50 per cent. aqueous potassium hydroxide, the chloride yields acetylene, ethylenedipiperidine, and 1-hydroxyethylpiperidine. Ethylenedipiperidine, $C_{12}H_{24}N_2$ (Brühl, *Ber.*, 1874, 4, 738), boils at 263° under 745 mm. pressure and is easily soluble in alcohol or ether. The *picrate*, $C_{12}H_{24}N_2 \cdot 2C_6H_3O_7N_3$, crystallises in long, rhombic needles, decomposes at 225°, and is soluble in 250 parts of boiling, or in 2300 parts of water at 15°. The aurichloride forms prismatic crystals and decomposes at about 207°; the platinichloride, $C_{12}H_{24}N_2 \cdot H_2PtCl_6$, crystallises in glistening, monoclinic leaflets and decomposes at 255°. The base reacts with ethylene dibromide to form a quaternary salt, which on conversion into the corresponding chloride is found to be identical with diethylenedipiperidinium chloride formed from 1-chloroethylpiperidine. Contrary to Marckwald and Frobenius's statement, the chloride remains unchanged when heated with concentrated hydrochloric acid at 100° for two hours.

G. Y.

Constitution of Histidine. F. KNOOP and ADOLF WINDAUS (*Beitr. chem. Physiol. Path.*, 1905, 7, 144—147).—*Glyoxaline-4-propionic acid*, $\begin{smallmatrix} NH \cdot CH \\ | \\ CH=N \end{smallmatrix} > C \cdot CH_2 \cdot CH_2 \cdot CO_2H$, may be synthesised by the

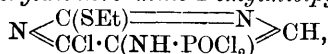
action of formaldehyde and ammonia on Wolff's glyoxypropionic acid (*Abstr.*, 1891, 416). It crystallises from dilute acetone in rectangular plates, decomposes at 208—209°, is readily soluble in water, less readily in alcohol, and is insoluble in ether or acetone. The *phosphotungstate* decomposes at a temperature above 300°; the *nitrate* crystallises in six-sided plates, is insoluble in ether, and decomposes at 143—148°; the *platinichloride* crystallises in yellowish-red cubes somewhat readily soluble in hot water, and melts and decomposes at

209°. The *hydrochloride* and *hydriodide* are readily soluble and the *mercuric* and *silver* salts insoluble. The *copper* salt crystallises from hot water in small blue needles. The same acid may be obtained by the reduction of Fränkel's hydroxydiaminohistidine (Abstr., 1903, i, 650) with red phosphorus and concentrated hydriodic acid at 150°. This method of formation is an additional argument in favour of Pauly's conclusion that histidine is an α -amino- β -glyoxaline-4-propionic acid (Pauly, Abstr., 1904, i, 1068). J. J. S.

Compound of Pyramidone with Mercuric Chloride. CHARLES ASTRE and G. BÉCAMEL (*Bull. Soc. chim.*, 1905, [iii], 33, 1084—1087).—When a solution of mercuric and sodium chlorides in water is added to a solution of pyramidone in water, a precipitate of an additive compound of pyramidone (1 mol.) with mercuric chloride (1 mol.) is formed. This melts at 157—158° and is soluble in alcohol, ether, or acetone. Its reactions with a number of reagents are given in the original. When the precipitation takes place in presence of hydrochloric acid, the *hydrochloride* of the additive compound separates. It melts at 197—198° and is slightly soluble in alcohol or ether, more so in acetone or water. These substances appear to be similar in constitution to the antipyrine compounds described by Schuyten (Abstr., 1898, i, 452) and unlike those obtained by Ville and Astre (Abstr., 1900, i, 362, 411). T. A. H.

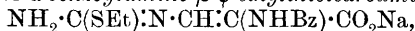
Pyrimidines : 5-Amino-6-oxy-2-ethylthiopyrimidine. XI. TREAT B. JOHNSON (*Amer. Chem. J.*, 1905, 34, 191—204).—By the condensation of ethyl formate with ethyl carbethoxyaminoacetate in presence of sodium, the *sodium* derivative of ethyl formylcarbethoxyaminoacetate is produced, which, when added to an aqueous solution of ψ -ethylthiocarbamide, yields *trans- α -carbethoxyamino- β - ψ -ethylthiocarbamideacrylic acid*, $\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{N}\cdot\text{C}(\text{SEt})\cdot\text{NH}_2$, which crystallises from hot water in colourless, microscopic prisms and decomposes at 259°; a yield of 40—46 per cent. of the theoretical was obtained. When this compound is dissolved in warm acetic anhydride, it is converted into *5-carbethoxyamino-6-oxy-2-ethylthiopyrimidine*, $\text{NH}\langle\text{C}(\text{SEt})=\text{N}\rangle\text{CH}$, which crystallises in prisms and melts at 189—190°. If either the acid or the pyrimidine just described is boiled with solution of sodium hydroxide, *5-amino-6-oxy-2-ethylthiopyrimidine*, $\text{NH}\langle\text{C}(\text{SEt})=\text{N}\rangle\text{CH}$, is obtained, which crystallises from hot water in groups of radiating needles and melts at 160°. When the *trans*-acid is boiled with dilute sodium hydroxide and the product, after being acidified with nitric acid, is treated with solution of silver nitrate, the *di-silver* salt of *5-carboxylamino-6-hydroxy-2-ethylthiopyrimidine*, $\text{N}\langle\text{C}(\text{SEt})=\text{N}\rangle\text{CH}$, is produced as an amorphous precipitate.

6-Chloro-5-phosphoryldichloroamino-2-ethylthiopyrimidine,



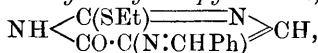
obtained by the action of phosphorus oxychloride on 5-amino-6-oxy-2-ethylthiopyrimidine, is a yellow, crystalline substance which decomposes at about 247—250°. When this compound is heated with alcoholic ammonia at 160—165° for three hours, 6-chloro-5-phosphoryltri-amino-2-ethylthiopyrimidine, $\text{N} \begin{smallmatrix} \text{C}(\text{SEt}) \\ \text{CCl} \cdot \text{C}[\text{NH} \cdot \text{PO}(\text{NH}_2)_2] \end{smallmatrix} \text{N} \rangle \text{CH}$, is formed, which has a green, metallic appearance, sinters at about 258°, decomposes at 290—300°, and is insoluble in water or the usual organic solvents.

When 5-benzoylamino-2-ethylthiol-6-oxypyrimidine (Johnson and Clapp, Abstr., 1904, i, 820) is boiled with solution of sodium hydroxide, the sodium salt of α -benzoylamino- β - ψ -ethylthiolcarbamideacrylic acid,



is obtained, which crystallises in needles, melts and decomposes at 124—125°, and is reconverted by acids into the pyrimidine.

5-Benzylideneamino-6-oxy-2-ethylthiopyrimidine,



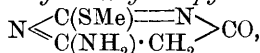
prepared by the action of benzaldehyde on 5-amino-6-oxy-2-ethylthiopyrimidine, crystallises from benzene in plates or prisms and melts at 185—187°.

5-Benzoylamino-2-thion-6-oxypyrimidine, $\text{NH} \begin{smallmatrix} \text{CS} \\ \text{CO} \cdot \text{C}(\text{NHBz}) \end{smallmatrix} \text{NH} \rangle \text{CH}$,

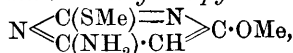
obtained by the action of thiocarbamide on the sodium derivative of ethyl hydroxymethylenehippurate, crystallises in plates, decomposes at 300—310°, and is insoluble in water or alcohol.

[By S. H. CLAPP.]—By the action of phosphorus oxychloride on 5-benzoylamino-2-ethylthiol-6-oxypyrimidine, 2-ethylthiol-5 : 6- μ -phenyl-oxazolinepyrimidine, $\text{SEt} \cdot \text{C} \begin{smallmatrix} \text{N} \\ \text{N} \cdot \text{CH} : \text{C} \cdot \text{N} \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{O} \\ \text{C} \cdot \text{N} \end{smallmatrix} \rangle \text{CPh}$, is produced as a white, crystalline solid, which melts at 108—109° and is reconverted by hydrochloric acid into the original pyrimidine; the hydrochloride melts and decomposes at 147°. E. G.

Pyrimidines: Action of Aqueous and Alcoholic Ammonia and Aniline on some Halogen- and Thiol-pyrimidines. X. TREAT B. JOHNSON and KARL O. JOHNS (*Amer. Chem. J.*, 1905, 34, 175—191).—6-Amino-4-oxy-2-methylthiopyrimidine,



obtained by the action of methyl iodide (1 mol.) on 6-amino-4-oxy-2-thiopyrimidine (Traube, Abstr., 1904, i, 632) in presence of sodium ethoxide (1 mol.), crystallises from hot alcohol in colourless plates and decomposes at 267°. If 2 mols. of methyl iodide and sodium ethoxide are used, 4-methoxy-6-amino-2-methylthiopyrimidine,

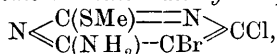


is produced, which crystallises from alcohol in long prisms and melts and decomposes at 256°. 5-Bromo-6-amino-4-oxy-2-methylthiopyrimi-

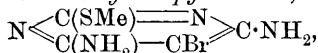
dine, $\text{N} \begin{smallmatrix} \text{C}(\text{SMe}) \\ \text{C}(\text{NH}_2) \cdot \text{CHBr} \end{smallmatrix} \text{N} \rangle \text{CO}$, crystallises in slender prisms, becomes

brown above 200° , and does not melt below 300° . 6-Amino-4-oxy-2-ethylthiopyrimidine, $\text{N} \begin{smallmatrix} \diagup \text{C}(\text{SEt})=\text{N} \\ \diagdown \text{C}(\text{NH}_2)-\text{CH}_2 \end{smallmatrix} \text{CO}$, prepared in the same manner as the corresponding methyl derivative, crystallises from water in long, slender prisms, is very soluble in alcohol, and melts at $216-217^{\circ}$.

4-Chloro-6-amino-2-methylthiopyrimidine, which was first obtained by Wheeler and Jamieson (Abstr., 1904, i, 940) by heating 4:6-dichloro-2-methylthiopyrimidine with alcoholic ammonia, can be prepared more easily by the action of phosphorus oxychloride on 6-amino-4-oxy-2-methylthiopyrimidine. When this chloro-compound is heated with concentrated aqueous ammonia at $185-195^{\circ}$ for five hours, 4:6-diamino-2-methylthiopyrimidine (Wheeler and Jamieson, *loc. cit.*) is formed, which is very stable and can be heated with a concentrated solution of ammonia, either aqueous or alcoholic, at $205-215^{\circ}$ without change. 4-Chloro-5-bromo-6-amino-2-methylthiopyrimidine,



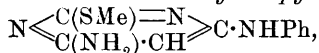
obtained by the action of bromine on 4-chloro-6-amino-2-methylthiopyrimidine, melts at 165° and is sparingly soluble in water; its *hydrobromide* melts at $180-190^{\circ}$ and decomposes at 208° . When this compound is heated with aqueous ammonia for four hours at $150-160^{\circ}$, 5-bromo-4:6-diamino-2-methylthiopyrimidine,



is produced, which crystallises from hot water in large prisms and melts at 192° . This substance is not obtained if alcoholic ammonia is substituted for the aqueous solution, and it is very stable in contact with either aqueous or alcoholic ammonia at $200-210^{\circ}$.

5-Bromo-6-amino-2-thion-4-oxypyrimidine, $\text{N} \begin{smallmatrix} \diagup \text{CS}=\text{NH} \\ \diagdown \text{C}(\text{NH}_2)\cdot\text{CHBr} \end{smallmatrix} \text{CO}$, obtained by the action of bromine on 6-amino-2-thion-4-oxypyrimidine, forms granular crystals, does not melt below 300° , and is sparingly soluble in acetic acid and insoluble in water.

When 4-chloro-6-amino-2-methylthiopyrimidine is heated with aniline (1 mol.), 6-amino-4-anilino-2-methylthiopyrimidine,



is produced, which crystallises from benzene in groups of microscopic prisms and melts at 124° ; the *dihydrochloride* melts and decomposes at 121° . If 2 mols. of aniline are employed, 6-amino-2:4-dianilinopyrimidine, $\text{N} \begin{smallmatrix} \diagup \text{C}(\text{NHPh})\text{:N} \\ \diagdown \text{C}(\text{NH}_2)\cdot\text{CH} \end{smallmatrix} \text{C}\cdot\text{NHPh}$, is formed, which melts at $65-70^{\circ}$ and is extremely soluble in the ordinary organic solvents; the *sulphate* melts and decomposes at $190-193^{\circ}$. 5-Bromo-6-amino-4-p-bromo-

anilino-2-methylthiopyrimidine, $\text{N} \begin{smallmatrix} \diagup \text{C}(\text{SMe})=\text{N} \\ \diagdown \text{C}(\text{NH}_2)-\text{CBr} \end{smallmatrix} \text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$,

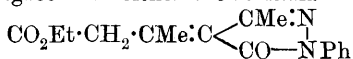
obtained by the action of bromine on 6-amino-4-anilino-2-methylthiopyrimidine, crystallises in long, slender prisms and melts at 202° ; the *hydrobromide* decomposes at 290° . This compound is also produced when 4-chloro-5-bromo-6-amino-2-methylthiopyrimidine is heated with *p*-bromoaniline.

4-Chloro-5-bromo-6-amino-2-oxypyrimidine, $\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}_2) \cdot \text{CBr} \end{smallmatrix} \text{CCl}$,

formed by the action of bromine on 4-chloro-6-amino-2-oxypyrimidine, crystallises from hot water in groups of microscopic prisms, becomes brown at 210° , and decomposes at about 230° ; the *hydrobromide* decomposes at $230\text{--}240^\circ$.

6-Chloro-2-ethylthiopyrimidine is unaffected by aqueous ammonia at $140\text{--}150^\circ$, but when heated with the reagent at $185\text{--}195^\circ$ is converted into 2:6-diaminopyrimidine. When 6-chloro-5-bromo-2-ethylthiopyrimidine (Wheeler and Johnson, *Abstr.*, 1904, i, 625) is heated with aqueous ammonia at $140\text{--}150^\circ$ or at $185\text{--}195^\circ$, 5-bromo-6-amino-2-ethylthiopyrimidine is produced. E. G.

Condensation of Ethyl Acetoacetate with Phenylmethylpyrazolone and the Products formed by the Action of Hydrazine and of Phenylhydrazine on Dehydracetic Acid. ROBERT STOLLÉ (*Ber.*, 1905, 38, 3023—3032. Compare Knorr, *Abstr.*, 1887, 678).—A condensation product, $\text{C}_{16}\text{H}_{18}\text{O}_3\text{N}_2$, of ethyl acetoacetate and phenylmethylpyrazolone is formed when the two substances are mixed, the water formed removed, and the mixture then heated on the water-bath for several hours. It is always accompanied by Knorr's lactone, melting at 145° , and crystallises from alcohol in glistening, yellow needles melting at 98° and readily soluble in ether, alcohol, or benzene. When heated at 150° , it loses alcohol and yields Knorr's lactone. With nitrous acid, it yields an *isonitroso*-derivative, $\text{C}_{16}\text{H}_{17}\text{O}_4\text{N}_3$, which crystallises from alcohol in slender, orange-red needles, melting and decomposing at about 198° . A *silver* derivative, $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_3\text{Ag}\cdot\text{AgNO}_3$, has been prepared. When hydrolysed with 2 per cent. aqueous sodium hydroxide, the condensation product yields Knorr's 1-phenyl-3-methyl-4-isopropylene-5-pyrazolone. When ethylated, the product yields the *ethoxy*pyrazolone derivative, $\text{C}_{18}\text{H}_{22}\text{O}_3\text{N}_2$, which crystallises from alcohol in glistening, hard prisms, melting at 117° , and is soluble in organic solvents, but insoluble in alkalis or acids. The reactions of the condensation product agree with either the formula

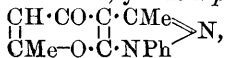


or the tautomeric formula $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH} \begin{smallmatrix} \text{CMe}\cdot\text{N} \\ \text{CO}\text{---}\text{NPh} \end{smallmatrix}$.

To Knorr's lactone, melting at 145° , is attributed the constitutional formula $\begin{smallmatrix} \text{CH}\cdot\text{CMe}\cdot\text{C}\cdot\text{CMe} \\ \text{CO}\cdot\text{O}\text{---}\text{C}\cdot\text{NPh} \end{smallmatrix} \text{N}$.

Ethyl ethylacetoacetate and phenylmethylpyrazolone, when heated at 160° , yield a *lactone*, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$, which crystallises in colourless needles melting at 142° .

The phenylhydrazone of dehydracetic acid (Perkin, *Trans.*, 1887, 51, 494), when heated with ether and acetyl chloride or with alcohol and concentrated hydrochloric acid, yields a *product*,



isomeric with Knorr's lactone. It crystallises in slender needles,

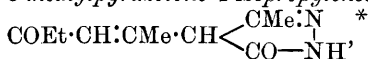
melts at 158° , and is insoluble in acids and alkalis. Mohr's phenyl-methylpyrazylphenylmethylpyrazolone melting at 260° is usually formed as a by-product (this vol., i, 676).

Dehydracetic acid and hydrazine hydrate react, yielding the *hydrazone*, $C_8H_{10}O_3N_2$. This crystallises in slender needles, turns yellow at 150° , melts and decomposes at 208° , dissolves in hot water, dilute acids, and alcohol, and reduces ammoniacal silver nitrate. Its *benzylidene* derivative, $C_{15}H_{14}O_3N_2$, crystallises in yellowish-green needles and melts at 191° .

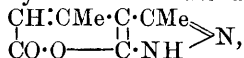
The *ketazine*, $C_{16}H_{14}O_6N_2$, is formed as a by-product in the preparation of the hydrazone, and is also formed when acid solutions of the latter are heated. It crystallises from acetic acid in yellowish-green needles, melts at 265° , dissolves sparingly in hot alcohol, and is insoluble in water, ether, or dilute acids.

Methylpyrazylmethylpyrazolone, $\begin{array}{c} \text{CMe} \cdot \text{CH} \\ \parallel \\ \text{N} - \text{NH} \end{array} \gg \text{C} \cdot \text{CH} \begin{array}{c} \text{CMe} \cdot \text{N} \\ \parallel \\ \text{CO} - \text{NH} \end{array}$, obtained by the action of an excess of hydrazine hydrate on dehydracetic acid, melts at 260° , and is soluble in alcohol and in alkalis. The *silver* salt has been prepared. J. J. S.

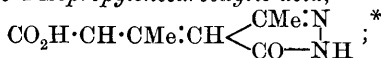
Azine of Ethyl Acetoacetate. LUDWIG WOLFF (*Ber.*, 1905, 38, 3036—3041. Compare *Abstr.*, 1904, i, 722, and Stollé, preceding abstract).—*Ethyl 3-methylpyrazolone-4-isopropylencarboxylate*,



is formed together with methylpyrazolone by the action of dilute ammonia on ethyl azoacetoacetate, also when the azine is boiled with 50 per cent. alcohol, but most readily by the action of aqueous sodium hydroxide on a mixture of methylpyrazolone and ethyl acetoacetate. It forms minute crystals from alcohol, dissolves in sodium carbonate solution and also in dilute hydrochloric acid, and gives a red coloration with ferric chloride. When rapidly heated, the ester decomposes at about 186° , yielding ethyl alcohol and the lactone,



which corresponds with Knorr's lactone melting at 145° . The same lactone is formed when ethyl azoacetoacetate is heated at 160 — 180° , or when molecular quantities of methylpyrazolone and ethyl acetoacetate are heated at 160 — 180° (compare Rosengarten, *Abstr.*, 1894, i, 546). When hydrolysed with cold sodium hydroxide solution, it yields *3-methylpyrazolone-4-isopropylencarboxylic acid*,



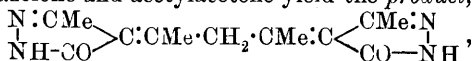
this melts at 145° , dissolves sparingly in water, alcohol, or ether, but readily in sodium carbonate or 10 per cent. hydrochloric acid. An

isomeric acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{C} \begin{array}{c} \text{CMe} \cdot \text{N} \\ \parallel \\ \text{CO} - \text{NH} \end{array}^*$, melting at 131° , is formed by the action of cold 10 per cent. sodium hydroxide on ethyl

* The position of the double linking in the side chain has not been determined with certainty.

azoacetoacetate. It is somewhat more stable than its isomeride, but both are decomposed into carbon dioxide and 3-methyl-4-isopropylene-pyrazolone, $C_7H_{10}ON_2$. The same products are formed when the acid melting at 145° is heated with alcohol or water at $60-70^\circ$. The pyrazolone derivative crystallises from alcohol in colourless prisms melting at $223-224^\circ$. It gives the ferric chloride reaction, and may be synthesised from acetone and methylpyrazolone in sodium carbonate solution.

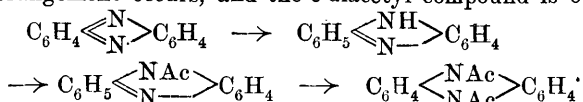
Methylpyrazolone and acetylacetone yield the product,



melting at 206° . It is insoluble in alkalis and gives no coloration with ferric chloride.

J. J. S.

Dihydroazines. OSCAR HINSBERG (*Ber.*, 1905, 38, 2800—2803. Compare Hinsberg and Garfunkel, *Abstr.*, 1897, i, 123; Tichwinsky and Wolochowitsch, this vol., i, 383).—Hinsberg and Garfunkel's *s*-diacetyldihydrophenazine is obtained when the monoacetyl compound is boiled for some time with acetic anhydride. It would thus appear that the primary dihydro-derivative has the unsymmetrical structure and yields a monoacetyl derivative, but that on further acetylating molecular rearrangement occurs, and the *s*-diacetyl compound is obtained.



This is used in support of the view of the quinonoid structure of phenazine and similar compounds (compare *Abstr.*, 1902, i, 238).

J. J. S.

Dihydrophenazine. WLADIMIR G. SCHAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 567—568).—The author objects to the unsymmetrical structure for phenazine given by Tichwinsky and Wolochowitsch (this vol., i, 383), the results obtained by the latter giving no definite indications on this head. Further, scarcely any analogy exists between the properties of the indulines and safranines and those of phenazine, the known properties of which do not support a quinonoid structure. The symmetrical formula for phenazine gives a much better explanation of the work of Wohl and Aue (*Abstr.*, 1901, i, 612), and of Wohl (*Abstr.*, 1904, i, 155), than the unsymmetrical one.

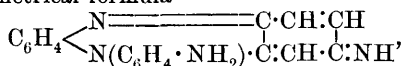
T. H. P.

Trihydroxyphenylrosinduline. KALLE & Co. (D.R.-P. 158101).—The preparation of trihydroxyphenylrosinduline (this vol., i, 554) may be modified by boiling the *p*-aminophenol and the naphthalene base together in aqueous solution or suspension in a reflux apparatus for 5—6 hours. A purer product is obtained than when fusion is employed.

C. H. D.

Unsymmetrical Safranines. PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1905, [iii], 33, 995—998. Compare Barbier and Vignon, *Abstr.*, 1888, 54, 141, 688).—Safranines are generally represented as having symmetrical constitutions, which, however,

does not agree always with their properties. That unsymmetrical safranines may exist is shown by the formation of phenosafranine by the oxidation of a mixture of 2:4'-diaminodiphenylamine and aniline hydrochlorides by potassium dichromate in neutral solution. It must have the unsymmetrical formula

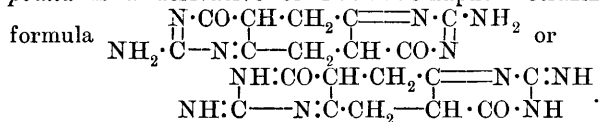


as the similar oxidation of a mixture of 2:4:4'-triaminodiphenylamine and aniline hydrochlorides leads to the formation of Ris' aminophenosafranine,

$\begin{array}{c} \text{CH} \cdot \text{CH} \text{-----} \text{C} \cdot \text{N} \text{=====} \text{C} \cdot \text{CH} \cdot \text{CH} \\ \text{C}(\text{NH}_2) \cdot \text{CH} \cdot \text{C} \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{NH}_2) \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{NH} \end{array}$ (Abstr., 1895, i, 148). The amino-group introduced by the aniline must assume, therefore, the *para*-position. G. Y.

Condensation of Ethyl Succinylsuccinate with Guanidine. Derivative of 1:3:6:8-Naphthatetrazine, a New Heterocycloid. MARSTON T. BOGERT and ARTHUR WAYLAND DOX (*J. Amer. Chem. Soc.*, 1905, 27, 1127—1140).—Ethyl *p*-diaminoterephthalate was prepared by Baeyer's method (Abstr., 1886, i, 445), which consists in converting ethyl succinylsuccinate into the di-imine, and oxidising the latter with bromine. The di-imine melts at 177—178°, and not at 181°, as stated by Baeyer. When the ester was treated with acetic anhydride, it dissolved, but no acetyl derivative could be isolated. The ester reacts with phenylcarbimide and with phenylthiocarbimide to form compounds which in general behaviour resemble the naphthatetrazine derivative described later. The product obtained with phenylthiocarbimide is yellow and very sparingly soluble in water or alcohol, but dissolves more readily in phenol, aniline, pyridine, or quinoline to form solutions with a yellowish-green fluorescence.

Ethyl succinylsuccinate does not react with carbamide or with phenylcarbimide. When the ester is heated with an alcoholic solution of guanidine thiocyanate or acetate in presence of sodium ethoxide, a yellowish-white precipitate is produced which is insoluble in water and most organic solvents, but is slightly soluble in alcohol. This compound is a derivative of 1:3:6:8-naphthatetrazine, and has the formula



When heated, it does not melt, but ammonia is evolved, and the mass becomes charred. The *hydrochloride* and *sulphate* are described. The *sodium* derivative crystallises with 6H₂O, and is strongly fluorescent; the *potassium* derivative was also prepared. E. G.

The Pyrrole-blue Group. CARL LIEBERMANN and G. HÄSE (*Ber.*, 1905, 38, 2847—2853. Compare Liebermann and Mauthner, Abstr., 1904, i, 684; Ciamician and Silber, Abstr., 1884, 740; Meyer and Stadler, *ibid.*, 1045).—Pyrrole-blue A, C₂₄H₁₈O₃N₄, is obtained as a blue precipitate when 5 grams of freshly distilled pyrrole are added to 10 grams of isatin dissolved in 5½ litres of water con-

taining 50 grams of concentrated sulphuric acid, and cooled to 5° with ice. The dry powder has an indigo-blue colour, cannot be purified by recrystallisation, and dissolves in concentrated sulphuric acid to form a violet solution which becomes bluish-black. When dissolved in pyridine and boiled with acetic anhydride, it yields only 6—12 per cent. of a derivative which is probably *acetylpyrrole-blue B*, $C_{24}H_{16}O_2N_4Ac_2$, derived from a small quantity of pyrrole-blue B present in the precipitate. It forms glistening, golden, microscopic needles, is soluble in hot pyridine or hot glacial acetic acid forming blue solutions, and dissolves in cold concentrated sulphuric acid to form a rosaniline-red solution which becomes blue; on immediate addition of water, the sulphuric acid solution deposits the unchanged acetyl derivative, but after the colour-change has taken place the precipitate consists of *acetylpyrrole-blue-B-disulphonic acid*, $C_{28}H_{20}O_4N_4(SO_3H)_2$. On evaporation of its blue, aqueous solution, this is obtained as a copper-coloured filament on the glass walls of the vessel. It dyes silk blue in aqueous solution, and forms a *barium* salt, $C_{28}H_{20}O_4N_4(SO_3)_2Ba$, on addition of barium chloride to its slightly ammoniacal solution. On warming the original sulphuric acid solution on the water-bath, a higher *sulphonic acid*, which is red and more easily soluble, is formed.

Pyrrole-blue B, $C_{24}H_{18}O_2N_4$, is formed when a solution of 0.75 gram of pyrrole in 10 c.c. of glacial acetic acid is added to a mixture of 100 c.c. of a 1 per cent. solution of isatin in glacial acetic acid and 40 c.c. of 15 per cent. sulphuric acid, cooled to 0° by ice-water; after five minutes, 10 c.c. of ice-water are added and the product filtered. After boiling the dried precipitate 3 to 4 times with pyridine, it is obtained as a glistening powder resembling cantharidin; it is less soluble than the A-blue, forms blue solutions in boiling glacial acetic acid or pyrrole, and, with concentrated sulphuric acid, gives a violet-red coloration which becomes blue, and on addition of water deposits *pyrrole-blue-B-disulphonic acid*, $C_{24}H_{16}O_2N_4(SO_3H)_2$.

Bromo-, dibromo-, and nitro-isatins form metallic, blue derivatives with pyrrole more easily than does isatin.

Tetrabromopyrrole-blue, $C_{24}H_{14}O_2N_4Br_4$, formed from dibromoisatin, is only sparingly soluble and reacts slowly with concentrated sulphuric acid.

1-Ethylpyrrole, 1-acetylpyrrole, indole, furfuraldehyde, and pyromucic acid do not form blue derivatives with isatin.

Schotten's isatin-blue from dipiperidylisatin (Abstr., 1891, 928, 1491) is not identical with Meyer's pyrrole-blue, as it gives a yellowish-brown coloration with concentrated sulphuric acid.

G. Y.

Reduction of Hydroxyazo-compounds to Aminophenols by Phenylhydrazine. GIUSEPPE ODDO and ERNESTO PUXEDDU (*Ber.*, 1905, 38, 2752—2755).—The reduction of hydroxyazo-compounds to aminophenols by means of phenylhydrazine proceeds in accordance with the scheme $OH \cdot R \cdot N : N Ph + 2NHPh \cdot NH_2 = OH \cdot R \cdot NH_2 + H_2NPh + 2C_6H_6 + 2N_2$, where R represents an aromatic group.

When benzeneazo-eugenol is heated with phenylhydrazine at 110—200°, 5-amino-eugenol, melting at 110°, is formed. Similarly,

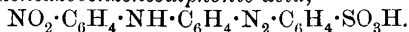
benzeneazo-*p*-cresol was reduced to the corresponding aminocresol, benzeneazocarvacrol to aminocarvacrol, and benzeneazophenol to *p*-aminophenol.
A. McK.

Velocity of Decomposition of *p*-Nitrobenzenediazonium Chloride. Reply to Cain. CARL SCHWALBE (*Ber.*, 1905, 38, 3071—3076. Compare this vol., i, 618, and Cain, *ibid.*, 724).—Further experiments confirm the view that the stability of the diazonium salt is decreased by the presence of free nitrous acid, by a high degree of concentration, by absence of mineral acids, and by the action of light. On the other hand, the stability is increased by excess of mineral acids or of mineral salts.

Full details of the method of titration of diazonium salts with β -naphthol are given.
J. J. S.

Reducing Action of Organo-magnesium Compounds. HARTWIG FRANZEN and W. DEIBEL (*Ber.*, 1905, 38, 2716—2718).—Hydrazobenzene is formed by the action of magnesium ethyl bromide on azobenzene, thus: $\text{NPh}\cdot\text{NPh} + 2\text{MgEtBr} = \text{MgBr}\cdot\text{NPh}\cdot\text{NPh}\cdot\text{MgBr} + \text{C}_4\text{H}_{10}$ and $\text{MgBr}\cdot\text{NPh}\cdot\text{NPh}\cdot\text{MgBr} + 2\text{H}_2\text{O} = \text{NHPh}\cdot\text{NHPh} + 2\text{MgBr}\cdot\text{OH}$. *p*-Azotoluene is reduced to *p*-hydrazotoluene in a similar manner. Benzylbenzylidenhydrazine is formed in similar manner from magnesium phenylbromide and benzaldazine; it was identified by means of its hydrochloride.
A. McK.

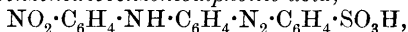
Nitro-derivatives of Orange IV. I and II. PAUL JUILLEARD (*Bull. Soc. chim.*, 1905, [iii], 33, 974—987, 987—994).—The dyes obtained by nitration of orange IV (anilinobenzeneazobenzene-*p*-sulphonic acid) may be divided into two classes: those, such as Indian yellow 15 and curcumine, which give orange to golden-yellow colours; and those, such as Indian yellow 25 and citronine, which dye wool and silk lemon-yellow shades. The dyes of the former group consist of mixtures of salts of three mononitro-derivatives of orange IV, along with *op'*- and *pp'*-dinitrodiphenylamines; those of the latter group contain salts of dinitro- and trinitro-derivatives of orange IV, along with dinitro-, trinitro-, and sometimes a little tetranitro-diphenylamines. The shade of yellow is influenced by the number of nitro-groups introduced into orange IV, but not by the *p* positions which they assume. Only those nitro-derivatives which are soluble in water are of value as dyes. When orange IV is treated with 1.5 mols. of nitric acid in cold glacial acetic acid solution, the principal product is *p*-nitroanilinobenzeneazobenzenesulphonic acid,



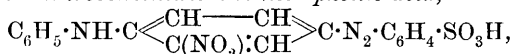
This is purified by successive treatment with cold glacial acetic acid and warm toluene, and finally by conversion into the *ammonium* or *potassium* salt. These crystallise from dilute ammonium or potassium chloride solutions in yellow needles, and yield the acid when treated with dilute hydrochloric acid. The *sodium* salt, $\text{C}_{18}\text{H}_{14}\text{O}_5\text{N}_4\text{SNa}\cdot 2\text{H}_2\text{O}$, crystallises in yellow needles and is moderately soluble in cold water. The acid forms a black, crystalline crust and is insoluble in cold water, but dissolves in boiling water to form a yellow solution which, on

addition of hydrochloric or sulphuric acid, gives a bluish-black solution and precipitate. With sodium nitrite, the acid forms a pale yellow *nitrosoamine* which is only sparingly soluble, and on nitration in the cold yields dinitrodiphenylnitrosoamine. With nitric acid in acetic acid solution, the potassium salt forms *p*-nitroanilino-*o*-nitrobenzeneazobenzenesulphonic acid and *pp'*-dinitrodiphenylamine.

o-Nitroanilinobenzeneazobenzenesulphonic acid,



and 4-anilino-3-nitrobenzeneazobenzenesulphonic acid,

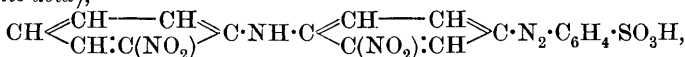


are obtained together by nitration of orange IV with 1 mol. of nitric acid in glacial acetic acid solution at 10–20°. The product is filtered and the filtrate treated with potassium chloride, which precipitates the *potassium* salts of the two *o*-nitro-acids along with a small quantity of dinitrodiphenylamines, which are removed by digestion with toluene. The potassium salts, which form isomorphic, rhombohedral crystals, can be separated by fractional crystallisation from dilute alcohol. The anilino-*o*-nitro-acid is very soluble in water, from its solution in which it is precipitated on adding hydrochloric or sulphuric acid as a brilliant yellow mass, and on treatment with nitric acid yields *p*-nitroanilino-*o*-nitrobenzeneazobenzenesulphonic acid. The *o*-nitroanilino-acid is less soluble in water, yields on addition of hydrochloric or sulphuric acid to its aqueous solution a black precipitate, which redissolves to form a violet solution in excess of acid, and on nitration forms *o*-nitroanilino-*o*-nitrobenzeneazobenzenesulphonic acid, *op'*-dinitrodiphenylamine, and diazobenzenesulphonic acid.

When nitrated in acetic acid solution, the nitroso-derivative of orange IV yields nitroso-4:8-dinitro- and nitroso-2:8-dinitro-orange IV along with *op'*- and *pp'*-dinitrodiphenylamines. After removal of the latter with excess of nitric acid and elimination of the nitroso-groups from the nitrosodinitro-acids by treatment with alcoholic sulphuric acid, the dinitro-acids are converted into their potassium salts, which are separated by fractional crystallisation. The two dinitro-acids are formed along with *op'*- and *pp'*-dinitrodiphenylamines and diazobenzenesulphonic acid by treatment of orange IV with 2 mols. of nitric acid in acetic or aqueous solution.

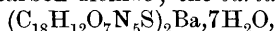
4:8-Dinitro-orange IV (4-*p*-nitroanilino-3-nitrobenzeneazobenzenesulphonic acid), $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C} \begin{array}{c} \text{CH} \text{---} \text{CH} \\ \text{C}(\text{NO}_2) \text{:CH} \end{array} \text{C} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, crystallises in slender, microscopic, yellow needles on addition of sulphuric acid to the aqueous solution of its potassium salt, $\text{C}_{18}\text{H}_{12}\text{O}_7\text{N}_5\text{SK} \cdot \text{H}_2\text{O}$. This crystallises in scarlet rhombohedra, is easily soluble in boiling, but only slightly so in cold water, and on nitration in acetic acid solution yields 2:4:8-trinitro-orange IV and *opp'*-trinitrodiphenylamine. The sodium salt, $\text{C}_{18}\text{H}_{12}\text{O}_7\text{N}_5\text{SNa} \cdot \text{H}_2\text{O}$, crystallises in small, orange, prismatic needles.

2:8-Dinitro-orange IV (4-*o*-nitroanilino-3-nitrobenzeneazobenzenesulphonic acid),



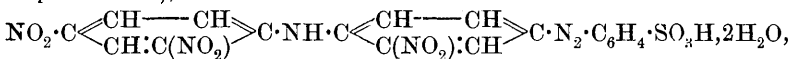
crystallises in orange needles, is easily soluble in water, and forms a *potassium* salt, $C_{18}H_{12}O_7N_5SK \cdot 2H_2O$, which crystallises in red flakes and is moderately soluble in boiling water; the *sodium* salt, $C_{18}H_{12}O_7N_5Na \cdot 3H_2O$, crystallises in long, thin, glistening plates. On nitration, 2:8-dinitro-orange IV and its salts form 2:4:8-trinitro-orange IV and *opp'*-trinitrodiphenylamine.

2:4-Dinitro-orange IV (*op*-dinitroanilinobenzeneazobenzenesulphonic acid), $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot SO_3H \cdot H_2O$, is formed by heating *op'*-dinitrobromobenzene with sodium aminobenzeneazobenzene-*p*-sulphonate in presence of sodium acetate. It separates in orange crystals on addition of sulphuric acid to the solution of its *sodium* salt. This ($3H_2O$) crystallises in orange-red prisms; the *potassium* salt (H_2O) crystallises in stellate groups of dark red prisms and is easily decomposed by carbon dioxide; the *barium* salt,



crystallises in orange needles. When evaporated with hydrochloric acid, these salts are hydrolysed into aminobenzeneazobenzenesulphonic acid and *op*-dinitrophenol. On nitration, the acid and its salts yield *opp'*-trinitrodiphenylamine and 2:4:8-trinitro-orange IV.

2:4:8-Trinitro-orange IV (4-*op*-dinitroanilino-3-benzeneazobenzene-sulphonic acid),



formed along with *opp'*-trinitrodiphenylamine melting at $188-189^\circ$, and *oo*-*p*-trinitrodiphenylamine melting at 184° , by nitration of orange IV or one of its dinitro-derivatives, crystallises in orange scales and is only slightly soluble in water. The *potassium* salt ($2H_2O$), crystallises in microscopic flakes and on drying forms a brilliant, dark greenish-brown mass.

2:4:6-Trinitro-orange IV (*oop*-trinitroanilinobenzeneazobenzenesulphonic acid), $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot SO_3H$, is formed by the action of picryl chloride on sodium aminobenzeneazobenzene-*p*-sulphonate in presence of sodium acetate. It is purified by recrystallisation of its *sodium* salt (H_2O), and when warmed with water decomposes into picric and aminobenzeneazobenzenesulphonic acids. The *potassium* salt (H_2O) crystallises in yellow flakes, and, when treated with nitric acid in cold acetic acid solution, yields a substance forming red crystals and picryl-*p*-nitroaniline. This, if the reaction is prolonged, is further nitrated to pentanitrodiphenylamine melting at 193° .

G. Y.

Disazo-dyes from 6-Amino- α -naphthol-3:7-disulphonic Acid. K. OEHLER (D.R.-P. 158147).—Disazo-dyes resembling those prepared from 6-amino- α -naphthol-3-sulphonic acid (Abstr., 1904, i, 809, and this vol., i, 162) may be prepared from 6-amino- α -naphthol-3:7-disulphonic acid, obtained by heating β -naphthylaminetrisulphonic acid with sodium hydroxide at 190° .

C. H. D.

Nature of Chemical and Electrical Stimulation. II. The Tension Coefficient of Salts and the Precipitation of Colloids by Electrolytes. ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1905,

14, 203—230).—The precipitation of colloidal albumin is brought about chiefly by an alteration in surface energy, and the precipitating power of an electrolyte is determined primarily by the solution tensions of the ions; ions of the same sign dissolve, and of the opposite sign precipitate, the colloid; their power is inversely proportional to the solution tension. W. D. H.

The Physical Units of Proteid Matter and the part played by Lime in their Coagulation. G. MALFITANO (*Compt. rend.*, 1905, 141, 503—504).—A solution of proteid matter consists of groups formed from complex organic matter associated with phosphates of the alkali or alkali earth metals in an acid or alkaline medium (compare this vol., ii, 14). From such a solution the proteid matter is precipitated by neutralisation, the precipitate always containing varying quantities of calcium phosphate. If, however, the nature of the groups is altered either by prolonged heating of the acid or alkaline solution, or by the action of a diastase, they are no longer precipitated by neutralisation, but are by the addition of large quantities of a normal salt, and they then contain acid or alkali phosphates and a less quantity of calcium phosphate. M. A. W.

Solubility of Globulin (Edestin) in Salt Solutions. THOMAS B. OSBORNE and ISAAC F. HARRIS (*Amer. J. Physiol.*, 1905, 14, 151—171).—Two forms of solution result where saline solutions are applied to edestin: (1) requires a large amount of salt; the edestin is precipitated unchanged from such a solution by water or dilute acids; (2) requires a small amount of salt; from such a solution the edestin is not precipitated by the reagents mentioned, and the anion has entered into combination with the proteid. Details are given for a large number of salts and their compounds with edestin.

W. D. H.

Composition of Proteid from Pine Seeds. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1905, 45, 473—478).—The proteid obtained from the seeds of *Picea excelsa* on hydrolysis with acids yielded glycine, 0·6; alanine, 1·8; pyrrolidine-2-carboxylic acid, 2·8; leucine, 6·2; glutamic acid, 7·8; aspartic acid, 1·8; phenylalanine, 1·2; serine, 0·08; tyrosine, 1·7 per cent.; also amino-valeric acid and tryptophan. W. D. H.

Composition of Conglutin from Lupin Seeds. EMIL ABDERHALDEN and J. B. HERRICK (*Zeit. physiol. Chem.*, 1905, 45, 479—485).—This proteid on hydrolysis with acids yielded glycine, 0·8; alanine, 2·5; aminovaleric acid, 1·1; leucin, 6·75; pyrrolidine-2-carboxylic acid, 2·6; phenylalanine, 3·1; glutamic acid, 9; and aspartic acid, 3 per cent. The analytical methods used are given at some length. W. D. H.

Osmotic Pressure of Hæmoglobin Solutions. E. WAYMOUTH REID (*J. Physiol.*, 1905, 33, 12—19).—The fairly constant osmotic pressure in relation to concentration in solutions of once-crystallised hæmoglobin, coupled with the appearances in the ultra-microscope,

leads to the conclusion that this substance when prepared by the methods described in the paper is in a true state of solution.

W. D. H.

Fluorides of Oxyhæmoglobin. ANTONY VILA and M. PIETRE (*Bull. Soc. chim.*, 1905, [iii], 33, 1083—1084. Compare this vol., i, 500, 622, and ii, 402).—If the new absorption band is due to methæmoglobin, as Ville and Derrien assert (this vol., i, 622), then it must be assumed that the addition of fluorides to oxyhæmoglobin converts the latter into methæmoglobin, since oxyhæmoglobin solutions show the same absorption band on the addition of fluorides. It is shown that the crystalline substance described by Ville and Derrien (*loc. cit.*) and supposed by them to be a fluorine compound of methæmoglobin is formed in the absence of fluorides and does not contain fluorine.

T. A. H.

The Origin of Cholehæmatin (Bilipurpurin). LEON MARCHLEWSKI (*Zeit. physiol. Chem.*, 1905, 45, 466—467. Compare Abstr., 1905, i, 500).—Cholehæmatin or bilipurpurin is identical with phylloerythrin. It is recommended that the last name be the one to be retained, as it indicates the origin of the substance from chlorophyll, and not from the blood or the bile.

W. D. H.

Preparation and Analysis of Nucleic Acids. VII. On the Nucleic Acid of the Spleen. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1905, 45, 370—380. Compare Abstr., 1903, i, 375, 668; 1904, i, 126; this vol., i, 105).—In the final stages of preparation of the nucleic acid, it is dissolved in excess of concentrated acetic acid and is freed from remaining impurities by precipitation from this solution by copper chloride or hydrochloric acid. The elementary composition of the acid from the spleen is but little different from those from other sources given previously. After hydrolysis, 100 grams yielded 8.3 of adenine picrate, 1.6 of guanine, 5.7 of thymine, 21.4 of cytosine picrate, and small quantities of uracil. By hydrolysis with 5 per cent. sulphuric acid, all the carbohydrate of the molecule is found as soluble decomposition products. If 2 per cent. acid is used, an insoluble substance is obtained in which the proportion of carbohydrate to pyrimidine bases is greater than in the original acid, although the absolute yield of lævulinic acid is lower than in hydrolysis of the nucleic acid. A melanin-like substance was also obtained by hydrolysis with strong mineral acids, as already described by Schmiedeberg and by Osborne and Harris.

W. D. H.

Composition of Gelatin impregnated with Potassium Dichromate and rendered Insoluble by Subsequent Exposure to Light. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], 33, 1032—1040. Compare Abstr., 1904, i, 210).—When gelatin, impregnated with potassium dichromate, is exposed to light, a portion of the salt is at once reduced with the formation of chromium sesquioxide and potassium hydroxide. The latter reacts with the excess of the dichromate to form potassium

chromate. This in turn is slowly reduced by the gelatin, forming more chromium sesquioxide, and finally chromium chromate is also probably formed by the action of chromium sesquioxide on the excess of potassium dichromate. In the first of these reactions the gelatin absorbs a constant quantity of about 3.5 per cent. of its weight of chromium sesquioxide to form the insoluble compound already described (*loc. cit.*). The amount subsequently absorbed increases with the concentration of the solution of dichromate used for impregnation and the duration of the subsequent exposure of the impregnated gelatin film to light, but the amount increases more slowly as the potassium chromate accumulates. The maximum amount of chromium compounds absorbed by the gelatin is equal to about 10 per cent. of chromium sesquioxide. Some chromium chromate appears to be formed when chromium sesquioxide is macerated in a solution of potassium dichromate in water. T. A. H.

Composition of Gelatin rendered Insoluble by Exposure to Light in Presence of Chromic Acid or Chromates. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], 33, 1040—1042. Compare preceding abstract).—Chromic acid and ammonium dichromate are both much more readily reduced by gelatin under the influence of light than is potassium dichromate. This is due to the fact that in the cases of the two former substances no stable salt corresponding with potassium chromate is formed. Analyses of the "insoluble gelatin" produced by the action of the foregoing substances and by other dichromates are tabulated in the original. It is noteworthy that in the cases of the dichromates of zinc, barium, lead, aluminium, and iron, the "insoluble gelatin" produced also contains a quantity of the oxide of the metal, the dichromate of which is used for impregnation. T. A. H.

Swelling of β -Gelatin. WOLFGANG OSTWALD (*Pflüger's Archiv*, 1905, 109, 277—288).—The name β -gelatin, which was first introduced by M. Traube for a 25 per cent. solution of gelatin which had been heated at 100° until it no longer set, is used by the author in a more general sense to include all gelatin solutions which have been heated. It is found that both the rate and intensity of swelling are greater for β -gelatin than for ordinary gelatin. When account is taken of the increased solubility at higher temperature and with prolonged heating, the curve obtained by plotting the intensity of swelling against the length of time during which the gelatin was heated is similar to that obtained by Schroeder for the viscosity (*Abstr.*, 1903, ii, 721).

The greater swelling capacity of plates of β -gelatin dried at 50° is not to be attributed to the fact that these plates contain a smaller amount of water than similar plates of ordinary gelatin.

β -Gelatin is more soluble than the ordinary, and this solubility begins at a given maximum swelling intensity, after which destruction of the microstructure of the plates probably occurs. J. J. S.

Organic Chemistry.

Mineral Oil from the Torbanite of New South Wales. JAMES M. PETRIE (*J. Soc. Chem. Ind.*, 1905, 24, 996—1002).—The relationship of torbanite to other bituminous minerals is discussed and its microscopic structure and composition recorded. It contains a very small quantity of natural oil (up to 0.3 per cent.) which can be extracted by prolonged agitation of the pulverised shale with ether. The natural oil resembles vaseline in consistency and has a reddish-brown colour with a dark green fluorescence. It solidifies at 30° and begins to boil at 160°; it has sp. gr. 0.9516 at 20°/4° and $n_{D^{20}}$ 1.5338 at 20°. It consists chiefly of saturated hydrocarbons.

The crude oil resulting from the destructive distillation of torbanite as well as the four fractions (naphtha, solar oil, heavy oil, and residue) obtained by treating the crude oil with sulphuric acid and then with sodium hydroxide and distilling, were subjected to fractional distillation. The volumes, specific gravities, refractive indices, bromine absorption, and substitution values, and in some cases the vapour densities of the various fractions are recorded.

The crude oil is a mixture chiefly of paraffins and olefines. The olefines form about 70 per cent. of the lightest distillate, but the proportion decreases as the boiling point rises, until at 280° the distillate consists almost entirely of paraffins.

The naphtha, which forms 9 per cent. of the crude oil, consists of approximately equal parts of paraffins and olefines with boiling points ranging from 30° to 200° and sp. gr. 0.660—0.800, the paraffins in this fraction ranging from pentane to undecane. The solar oil forms 54 per cent. of the crude oil, boils from 200—270°, and the sp. gr. ranges from 0.800—0.870. It contains 50 per cent. of paraffins in the lightest portion, the proportion increasing to 80 per cent. in the fraction distilling at 270°. The paraffins included range from dodecane to pentadecane.

The heavy oil constitutes 17 per cent. of the crude oil. The lightest portion, boiling between 270° and 300°, contains the last traces of the olefines, together with penta- and hexa-decanes. The paraffins $C_{17}H_{36}$ to $C_{30}H_{62}$ represent the oil boiling above 300°. Chrysene appears at the end of the distillation.

Minute quantities of benzene and its homologues were detected in the crude oil, together with a notable quantity of phenols and a trace of thiophen, and nearly all the distillates deposited pyrrole-red on standing.

The behaviour towards mixtures of sulphuric and nitric acid and the high sp. gr. of the distillates point to the presence of naphthenes in the oil.

H. M. D.

Incomplete Combustion of Gases. Cause of the Luminosity of Flame. WILHELM MISTELI (*Chem. Centr.*, 1905, ii, 1075; from *J. Gasbel*, 48, 802—804. Compare Tanatar, *Abstr.*, 1901, ii, 13, 228).—By the explosion of mixtures of ethylene and electrolytic

gas, the hydrocarbon is resolved into its elements, and traces of methane and acetylene are formed, whilst the oxygen combines with the elements of the hydrocarbon, forming carbon monoxide and hydrogen, carbon monoxide and water, or carbon dioxide and water, according to the proportion present. Explosion only takes place when the requisite quantity of oxygen is present, and the presence of 33 per cent. of ethylene prevents it. Similar results are obtained, broadly speaking, by the incomplete combustion of propylene, acetylene, and methane. The explosion of mixtures of propylene and electrolytic gas occurs when two volumes of oxygen are present, marsh gas and traces of acetylene being formed. The presence of 18 per cent. of propylene completely inhibits combustion. The phenomena appear in this case to be affected by the shape of the explosion vessel.

The explosion of acetylene and electrolytic gas is not dependent on the proportions of the gases, and traces of methane are formed. Acetylene, propylene, and ethylene are decomposed by the action of the electric spark; methane is also decomposed, but with much greater difficulty. The more readily the gas is itself decomposed, the less is the proportion of electrolytic gas required for explosion. Mixtures containing methane behave like those containing propylene and do not explode when 0.5, 1.5, or 2 volumes of oxygen are present; combustion is prevented by the presence of 32 per cent. of the hydrocarbon. Traces of acetylene are formed by the explosion.

In mixtures containing ethylene and acetylene, which are just explosive, the whole of the hydrogen is in the free state, and in the case of the other hydrocarbons almost all the hydrogen is free. The oxygen does not react with the hydrocarbons as such, but combines only with the products of their decomposition. The effect of the hydrocarbons on the inflammability of electrolytic gas depends therefore on their decomposition, the carbon then combining with the oxygen to form carbon monoxide.

Hydrogen cannot be accurately estimated in mixtures of hydrogen and methane or its homologues by explosion, since small quantities of the former escape combustion, but the palladium methods of Winkler, Bunte, and Hempel give accurate results. The hydrogen in mixtures containing hydrocarbons can only be estimated by combustion when but one saturated hydrocarbon of known composition is present.

E. W. W.

Preparation of Halogen Alkyls. RUDOLF F. WEINLAND and KARL SCHMID (*Ber.*, 1905, 38, 3696. Compare this vol., i, 557).—The method of preparing methyl chloride by heating dry sodium chloride with methyl sulphate has been already described by Dumas (*Ann. Chim. Phys.*, 1835, 58, 36).

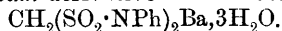
E. F. A.

Preparation of Pure Ethyl Alcohol. LUDWIG W. WINKLER (*Ber.*, 1905, 38, 3612—3616).—To prepare pure ethyl alcohol, commercial absolute alcohol is shaken with small quantities of finely-divided silver oxide and potassium hydroxide, at the ordinary temperature, for some days, until it does not reduce ammoniacal silver solution, then boiled with 20 grams of calcium filings per litre for

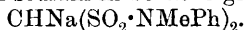
some hours, and finally distilled. The distillate contains about 0.1 per cent. of water, which may be removed by repeating the distillation with calcium filings. The ethyl alcohol so obtained boils at 77.81° under 743.5 mm., or at 78.2° under 754.9 mm., or at 78.29° under 757.8 mm. pressure, and is less hygroscopic than usually stated, as when exposed to the air in an open beaker for 15 minutes, it absorbs less than 0.1 per cent. of water. G. Y.

Methionie [Methanedisulphonic] Acid. GEORG SCHROETER and GUSTAV HERZBERG (*Ber.*, 1905, 38, 3389—3393).—*Methyl methane-disulphonate*, $\text{CH}_3(\text{SO}_3\text{Me})_2$, obtained from the silver salt and methyl iodide in ethereal or chloroform solution, forms long, white needles, melts at 47° , and is easily hydrolysed by water. The *ethyl* ester is an oil which does not solidify. By acting with potassium and methyl iodide on the methyl or ethyl ester and hydrolysing the product, *barium methylmethionate [ethane-aa-disulphonate]*, $\text{CHMe}(\text{SO}_3)_2\text{Ba}$, is obtained; using ethyl iodide in place of methyl iodide, *barium ethylmethionate [propane-aa-disulphonate]* is formed.

Methanedisulphonic chloride, $\text{CH}_2(\text{SO}_2\text{Cl})_2$, obtained by the interaction of methanedisulphonic acid and phosphorus pentachloride, boils at 135° under 10 mm. pressure, has a sp. gr. 1.821 at 22° , and solidifies only at low temperatures; it sometimes changes into a solid modification, which melts at about 60° , and is reconverted by distillation into the form melting at low temperatures. The chloride attacks alcohols vigorously, but does not give rise in this case to normal esters. With ethyl aminoacetate, a well-defined crystalline *methanedisulphonyl ethylaminoacetate*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, is obtained, which melts at 113.5° . With aniline, the *anilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NHPh})_2$, is produced; it forms lustrous, white crystals, melts at $192\text{--}193^{\circ}$, and gives a well-defined crystalline *sodium* derivative and a *barium* derivative,



On digesting the alkaline solution of the anilide with methyl sulphate *methanedisulphonylbisethylaniline*, $\text{CH}_2(\text{SO}_2\cdot\text{NMePh})_2$, is obtained; it crystallises from alcohol in needles and prisms, melts at $141.5\text{--}142.5^{\circ}$, and with sodium in benzene gives the *derivative*



The *compound*, $\text{CH}_2(\text{SO}_2\cdot\text{NEtPh})_2$, is obtained by ethylating the anilide with ethyl sulphate or with ethyl bromide at $100\text{--}120^{\circ}$, or by the action of ethylaniline on the chloride; it crystallises from alcohol and melts at $112\text{--}114^{\circ}$. In benzene solution it interacts with sodium to form a *sodium* derivative, $\text{CHNa}(\text{SO}_2\cdot\text{NEtPh})_2$, which combines with ethyl bromide or iodide giving *propane-aa-disulphonylbisethylaniline*, $\text{CHEt}(\text{SO}_2\cdot\text{NEtPh})_2$; this crystallises from alcohol in thick, transparent prisms, melts at 135° , and when heated with hydrochloric acid at $180\text{--}200^{\circ}$ gives ethylaniline and *propane-aa-disulphonic acid*, $\text{CHEt}(\text{SO}_3\text{H})_2$; the *barium* salt of the latter, $\text{CHEt}(\text{SO}_3)_2\text{Ba}, 3\text{H}_2\text{O}$, forms lustrous scales.

Methanedisulphonylbisphenetidine, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, melts at 221° , the *diethyl* derivative at $141\text{--}142^{\circ}$, *propane-aa-disulphonylbisethyphenetidine*, $\text{CHEt}(\text{SO}_2\cdot\text{NEt}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, at $93.5\text{--}94.5^{\circ}$.

W. A. D.

New Method of Preparing Esters. WILLIAM W. TAYLOR (*Proc. Roy. Soc. Edin.*, 1905, 25, 831—834).—The yields obtained in the preparation of esters are frequently unsatisfactory in consequence of the hydrolysing action of the water formed. In the method described for the preparation of ethyl esters, the water produced is removed by addition of benzene and distillation of the ternary mixture, ethyl alcohol, benzene, and water (compare Young, *Trans.*, 1902, 81, 707). In the actual working of the process, the dry acid is mixed with an excess of ethyl alcohol, and after addition of 1 c.c. of alcoholic hydrogen chloride, the solution is boiled for 20—30 minutes in a flask provided with a very efficient fractionating column and a tap funnel. A quantity of benzene sufficient to remove one-quarter of the water produced in the reaction is then run in, together with a little ethyl alcohol, and the ternary mixture distilled off. As soon as all the benzene has come over, distillation stops. This process is repeated three times. The residue is then free from water and is transferred to a fractionating flask and distilled under reduced pressure. The method has given good results in the preparation of ethyl tartrate, oxalate, succinate, and benzoate. H. M. D.

Metallic Formates and Acetates. ETTORE COLONNA (*Gazzetta*, 1905, 35, ii, 224—228).—*Stannous acetate*, $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$, prepared by boiling 100 c.c. of 98 per cent. acetic acid in a reflux apparatus with 90 grams of finely-granulated tin, distils in the form of a feathery mass of long, silky needles, softening at 170° , melting at 181 — 182° , and boiling at about 238 — 240° ; it dissolves in acetic acid, giving a solution which gradually becomes gelatinous.

Stannous formate, $\text{Sn}(\text{CHO}_2)_2$, separates in white, silky plates having the form of either a hexagon or parallelogram; it softens at 140 — 150° and then melts and decomposes. In contact with air, it assumes a yellow colour.

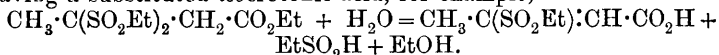
Bismuth acetate, $\text{Bi}(\text{C}_2\text{H}_3\text{O}_2)_3$, prepared by protracted boiling of acetic acid with bismuth, separates in hexagonal plates, dissolves in acetic acid, and decomposes without melting.

Bismuth formate, $\text{Bi}(\text{CHO}_2)_3$, separates in flocks of silky needles and decomposes without melting. T. H. P.

Insoluble Basic Aluminium Acetate. RUDOLF REISS (D.R.-P. 160348).—The basic acetates prepared by heating solutions of aluminium acetate are variable in composition and properties. An insoluble product of constant composition, containing 72 per cent. of acetic acid, is obtained by boiling a 5—15 per cent. solution of aluminium acetate, strongly acidified with acetic acid. The product separates rapidly in a dense form. The same basic acetate is obtained when a neutral 15 per cent. solution of aluminium acetate is heated in an autoclave. C. H. D.

Sulphonalcarboxylic Acids, and the Physiological Activity of Acid and Basic Derivatives of Sulphonal. THEODOR POSNER (*Chem. Zeit.*, 1905, 29, 1107—1108).—After giving a summary of the

results already published by himself, Baumann, and Autenrieth on the properties of α - and β -disulphone-carboxylic acid, the author draws a comparison between β -ketonic acids and β -disulphone-carboxylic acids, pointing out that whereas the former on hydrolysis yield either ketones or acids, the latter lose a sulphone group leaving a substituted *isocrotonic* acid, for example,

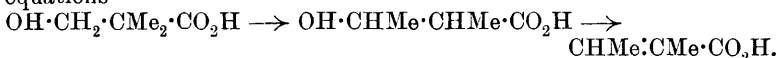


This decomposition does not, however, take place when the two hydrogens attached to the α -carbon atoms are replaced by alkyl groups.

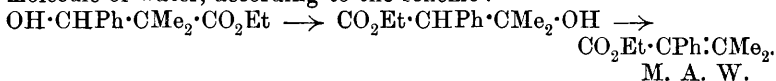
The physiological properties of these substances are such as to render them useless for therapeutic purposes. P. H.

Molecular Transpositions and Migration of Carboxyl Group in the Dehydration of Certain Hydroxy-acids.

EDMOND E. BLAISE and A. COURTOT (*Compt. rend.*, 1905, 141, 724—725. Compare Abstr., 1903, i, 604; 1904, i, 366, 796).—When ethyl hydroxypivalate [ethyl β -hydroxy- α -dimethylpropionate] is treated with a dehydrating agent, a mixture of ethyl tiglate and angelate is obtained; this reaction involves a molecular transposition whereby a methyl group and a hydrogen atom change places, and the elements of a molecule of water are removed, according to the equations



When ethyl β -phenyl- α -dimethylhydracrylate is treated with phosphoric oxide, it is converted into ethyl dimethylatropate [ethyl α -phenyl- β -dimethylacrylate], the molecular transposition involved in this reaction is a change of places between the carbethoxy- and hydroxyl groups, with the subsequent elimination of the elements of a molecule of water, according to the scheme:



Thallium Oxalates. RICHARD ABEGG and JAMES F. SPENCER (*Zeit. anorg. Chem.*, 1905, 46, 406—414).—The solubility of thallous oxalate at 25° was determined, and also the change of solubility caused by the addition of thallium nitrate and of potassium oxalate. In accordance with the Nernst theory, the solubility in presence of thallium nitrate diminishes owing to the increase of the thallium ions; it diminishes also at first in presence of small quantities of potassium oxalate, but afterwards increases considerably, owing to the formation of a complex salt. Attempts to determine the ionic concentration of the Tl^+ ion failed, but the $\text{C}_2\text{O}_4^{2-}$ concentration was determined with the aid of Schäfer and Abegg's $\text{Ag} | \text{Ag}_2\text{C}_2\text{O}_4$ electrode. This electrode in a solution of 0.5 mol. $\text{K}_2\text{C}_2\text{O}_4$ (containing, according to its conductivity, 0.288 mol. $\text{C}_2\text{O}_4^{2-}$) has an *E.M.F.* of +0.143 volt against a 1/10-normal electrode. The following

formula is used to calculate the C_2O_4'' concentration x of the solutions from the *E.M.F.* ϵ opposed to the 1/10 normal electrode :

$$0.143 - \epsilon = 0.0295 \log(x/0.288).$$

The solubility product $(TI')^2(C_2O_4'')$ was thus found $= 1.38 \cdot 10^{-5}$, and the stability constant $k = TI'C_2O_4'/TI'C_2O_4'' = 108$.

The solubility curves for mixtures of thallous oxalate, with thallium nitrate and potassium oxalate respectively are given, together with calculations of the ionic concentration in certain selected cases.

Quantitative experiments showed that even concentrated solutions of potassium oxalate dissolve very little thallic oxalate, so that the tendency to the formation of complex ions is small. Attempts to determine the TI''' concentration from measurements of the oxidation potential failed, but incidentally showed that the thallic salt is self-reducing at the expense of the oxalate ions. The vigorous evolution of carbon dioxide is easily shown on warming a flask in which moist thallic oxalate has been placed; at the same time, white thallous oxalate and brown thallic hydroxide are formed.

D. H. J.

Esterification Experiments. ALEX. D. BOGOJAWLENSKY and J. NARBUTT (*Ber.*, 1905, 38, 3344—3353).—The effect of the introduction of various metallic salts on the esterification of organic acids by ethyl alcohol has been studied. The salts employed were ferrous, zinc, cobalt, cupric, sodium, manganous, and nickel sulphates, also potassium pyrosulphate and chabazite.

Experiments made with succinic acid, using the acid, sulphate, and alcohol in the proportions 1 : 1.25 : 4 and boiling for about four hours, show that as regards their efficiency the salts may be arranged in the order ferrous, nickel, cupric, manganous, cobalt, and zinc sulphates. Sodium sulphate has no accelerating action. Copper sulphate accelerates the esterification of other aliphatic acids such as acetic, *n*-butyric, *isovaleric*, and citric acids; the acceleration is further increased by the addition of a little free sulphuric acid. Potassium pyrosulphate gives extremely good results with aromatic acids such as benzoic, salicylic, *o*-nitrobenzoic, gallic, cinnamic, and mandelic acids, whereas copper sulphate is not advantageous. The sulphates were dehydrated at 100°; their action may be partly due to their hygroscopic nature and partly to the small amount of free acid to which they give rise.

Copper sulphate is of no use for the esterification of trimethylcarbinol with acetic acid. Salol cannot be obtained by using potassium pyrosulphate and α - and β -naphthols cannot be esterified by this reagent.

J. J. S.

Tetra-amminechromium Salts. PAUL PFEIFFER (*Ber.*, 1905, 38, 9352—3601. Compare this vol., i, 33).—[With S. BASCI].—Chloro-aquotetra-amminechromium chloride (Jørgenson, *Abstr.*, 1890, 1213) is formed by the action of 25 per cent. aqueous ammonia on diaquodihydroxylodipyridinechromium chloride (*Abstr.*, 1902, i, 729) at 45—48°, and treatment of the resulting solution with concentrated hydrochloric acid; with ammonium sulphate in aqueous solution, it yields the characteristic oxalate; with potassium oxalate, the *oxalate*,

$[(\text{NH}_3)_4\text{Cr}(\text{H}_2\text{O})\text{Cl}]\text{C}_2\text{O}_4$, which separates in violet crystals, gives a precipitate of calcium oxalate with calcium chloride in aqueous solution, and yields silver chloride quantitatively when boiled with silver nitrate in nitric acid solution.

Bromo-aqua-tetra-amminechromium bromide (Cleve) is formed by the action of 25 per cent. aqueous ammonia and concentrated hydrobromic acid on diaquodihydroxylodipyridinechromium chloride; it forms violet, glistening crystals, and with potassium oxalate in aqueous solution yields a violet precipitate.

Oxalatotetra-amminechromium iodide, $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{I}\cdot\text{H}_2\text{O}$, is formed by the successive action of ammonium oxalate and potassium iodide on chloro-aqua-tetra-amminechromium chloride in aqueous solution; it crystallises in stout, glistening, orange-red prisms, loses H_2O over phosphoric oxide in a desiccator, and gradually decomposes at 100° . The *bromide*, $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{Br}\cdot\frac{1}{2}\text{H}_2\text{O}$, is formed by the action of concentrated hydrobromic acid on the nitrate; it crystallises in orange leaflets and dissolves in water to form an orange solution, which becomes green when warmed.

The action of ammonium oxalate and hydrobromic acid on chloro-aqua-tetra-amminechromium chloride leads to the formation of Cleve's triamminechromium oxalate.

Oxalatotetra-amminechromium chloride, $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{Cl}$, is formed by the action of concentrated hydrochloric acid on the nitrate in aqueous solution; it crystallises in glistening, orange leaflets, does not form a precipitate with calcium chloride in aqueous solution at the ordinary temperature, but is decomposed by boiling calcium chloride solution, and gives a precipitate with silver nitrate in nitric acid solution at the ordinary temperature. In concentrated aqueous solution, the chloride forms precipitates with platinic chloride, potassium dichromate and chromate, sodium dithionate, potassium iodide, and concentrated nitric acid. The *nitrate*, $[(\text{NH}_3)_4\text{CrC}_2\text{O}_4]\text{NO}_3\cdot\text{H}_2\text{O}$, is formed by the successive action of ammonium oxalate and potassium nitrate on chloro-aqua-tetra-amminechromium chloride; it crystallises in glistening, orange-red needles, is less soluble in water than are the bromide and chloride, and in concentrated solution forms with potassium chromate or dichromate a precipitate consisting of glistening, orange needles, and, with potassium iodide, stout, orange crystals. When warmed with concentrated hydrochloric or hydrobromic acid, the nitrate dissolves to form red solutions which, on cooling, deposit chloro-aqua-tetra-amminechromium chloride and bromo-aqua-tetra-amminechromium bromide respectively.

G. Y.

Syntheses with Ethyl Sodiomalonate and Similar Compounds. ARTHUR MICHAEL (*Ber.*, 1905, 38, 3217—3234. Compare this vol., i, 195, 506).—The action of ethyl chloroacetate on ethyl sodiomalonate in ethereal solution leads to the formation of a colourless, neutral solution and a precipitate consisting of sodium chloride, but in benzene solution, slowly at the laboratory temperature, more quickly on boiling, to the formation of a reddish-yellow, neutral solution, which is slightly opalescent in transmitted light, together with only traces of sodium chloride. This solution decomposes with

separation of sodium chloride, rapidly on addition of traces of water, or more slowly on treatment with methyl or ethyl alcohol; it decomposes to only a slight extent at 150° in a sealed tube, whilst at 200° sodium chloride separates quantitatively. It is not attacked by anhydrous carbon dioxide, but is decomposed with formation of sodium chloride when treated with hydrogen chloride; it yields sodium chloride together with a small quantity of a *substance* which crystallises in groups of needles when treated with glacial acetic acid, and it is decomposed also by the action of acetyl chloride, iodine, or silver benzoate. The yellowish-red, viscid liquid, $C_{11}H_{18}O_6ClNa$, obtained on evaporating the solution at 40° and finally on the water-bath, decomposes slowly in a vacuum at the laboratory temperature, more quickly at 100° .

The *additive* compound of ethyl chloroacetate and ethyl sodioethylmalonate, $C_{13}H_{22}O_6ClNa$, is formed in ethereal or benzene solution; the viscid, red oil obtained on evaporation decomposes with formation of sodium chloride when treated with absolute methyl or ethyl alcohols, more slowly with ethyl acetate or chloroform. The neutral ethereal solution is yellow and opaque by reflected, chrome-yellow by transmitted light, is only slowly decomposed at 100° in a sealed tube, but decomposes immediately on addition of traces of water; the yellow neutral benzene solution becomes orange at the ordinary temperature, or red when heated on the water-bath, and is decomposed by moisture, iodine, acetyl chloride, or hydrochloric acid.

The action of ethyl chloroacetate on ethyl sodiomethylmalonate in benzene solution leads to the formation of a yellow solution, which becomes orange when heated on the water-bath and on evaporation yields a viscid oil. The *additive* compound of ethyl chloroacetate and ethyl sodiopropylmalonate is formed in ethereal benzene solution, and, on evaporation, is obtained as a red, viscid oil. These derivatives of methyl- and propyl-malonic acids have properties resembling those of the corresponding ethyl compound.

The action of ethyl chloroacetate on ethyl sodioacetoacetate in warm ethereal solution leads to the formation of sodium chloride, but in benzene solution to the formation of a slightly alkaline orange solution, which deposits sodium chloride on addition of traces of water, but only slowly on treatment with methyl or ethyl alcohol, ether, ethyl acetate, or chloroform. The *additive* compound is obtained on distillation of the benzene and heating the residue at 110° under 12 mm. pressure as a viscid, orange, slightly milky liquid, which dissolves unchanged in benzene, but is less stable towards methyl or ethyl alcohol, ether, ethyl acetate, or chloroform than are the corresponding malonate derivatives.

The *additive* compound of ethyl chloroacetate and ethyl sodioethylacetoacetate is formed in ethereal solution and is obtained, on evaporation, as a red, viscid liquid; it is decomposed immediately by water, but dissolves in methyl alcohol or ethyl acetate to form a clear solution which decomposes only gradually.

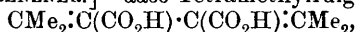
Comparative experiments show that the action of alkyl iodides on sodio-derivatives of ethyl acetoacetate or malonate, as expressed by the changes of temperature, takes place more rapidly than on sodium alkoxides. Of the results given, the following may be quoted in

illustration. An excess, 5.8 grams, of methyl iodide was added to 0.95 gram of sodium in 12.5 grams of propyl alcohol I; to 0.49 gram of sodium in 10 grams of ethyl alcohol together with 2.5 grams of ethyl lactate II; to 0.36 gram of sodium in 10 grams of ethyl alcohol together with 2.5 grams of ethyl malonate III; to 0.31 gram of sodium in 10 grams of ethyl alcohol together with 2.5 grams of ethyl ethyl-malonate IV, and the temperature taken at intervals after mixing.

Minutes after mixing.	I.	II.	III.	IV.
2	2°	1°	32°	10°
4	6	2	28	25
6	22	3	24	23
10	41	6	19	19
20	25	8.5	10	10
30	17	8	7	7

G. Y.

Butadiene Compounds. VII. The Colour of the Fulgenic Acids and Fulgides. HANS STOBBE (*Ber.*, 1905, **37**, 3673—3682). —[With ALFRED LENZNER.]—*aaδδ*-Tetramethylfulgenic acid,



prepared by the gradual addition of a mixture of ethyl teraconate and acetone to a suspension of sodium ethoxide in ether, is a colourless, crystalline compound melting and decomposing at 230°. *Tetramethyl-*

fulgide, $\text{CMe}_2\cdot\text{C}\cdot\text{CO} > \text{O}$, formed by dissolving the corresponding acid in cold methyl chloride, crystallises in colourless plates melting at 59.5°.

[With ROBERT ROSE and FERDINAND GADEMANN.]—*δ*-Phenyl-*aaδ*-trimethylfulgenic acid crystallises in colourless needles or six-sided prisms melting at 208—210°; at the same time a stereoisomeride melting at 221—223° is formed, which yields a more easily soluble barium salt. *δ*-Phenyl-*aaδ*-trimethylfulgide crystallises from light petroleum in citron-yellow needles melting at 132—133°.

[With ALFRED LENZNER.]—*δδ*-Diphenyl-*aa*-dimethylfulgenic acid, $\text{CPh}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CMe}_2$, is obtained as a colourless substance, which, on heating, softens at 188° and melts and decomposes at 201°; the *ester acid* crystallises in colourless prisms, which melt and decompose at 137.5°. *δδ*-Diphenyl-*aa*-dimethylfulgide crystallises in six-sided, citron-yellow plates melting at 171.5°. *aaδδ*-Tetraphenylfulgenic acid, prepared from benzophenone and ethyl diphenylitaconate, was not obtained pure; the corresponding *tetraphenylfulgide* crystallises in blood-red, triclinic crystals melting at 219°; at the same time, a bright red, rhombic isomeride is formed. E. F. A.

Butadiene Compounds. VIII. Colourless Alkylfulgides. HANS STOBBE and KARL LEUNER (*Ber.*, 1905, **38**, 3682—3685).—*δδ*-Dimethyl-*α*-isopropylfulgenic acid, $\text{CMe}_2\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CH}\cdot\text{CHMe}_2$, prepared by the condensation of isobutyraldehyde and ethyl tetraconate, is a colourless, crystalline compound melting and decomposing at 226°. *δδ*-Dimethyl-*α*-isopropylfulgide, formed on dissolving the acid in acetyl chloride, crystallises in colourless platelets melting at 72°. E. F. A.

Mixed Derivatives of *d*-Camphoric Acid and β -Campholide.

ALBIN HALLER and GUSTAV BLANC (*Compt. rend.*, 1905, 141, 697—701).— *α -Methyl camphorate β -chloride*, $\text{COCl} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Me}$, prepared by the action of phosphorus trichloride or thionyl chloride on *α -methyl β -hydrogen camphorate*, is a colourless, mobile liquid, which decomposes into camphoric anhydride and methyl chloride on distillation, is converted quantitatively into dimethyl camphorate by the action of methyl alcohol, reacts with ammonia to form *α -methyl β -camphoramate*, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Me}$, a white, crystalline substance, melting at 139° , having $[\alpha]_D + 57^\circ 15'$ at 27° , soluble in alcohol, and sparingly soluble in water; and with phenylhydrazine to form *α -methyl β -phenylhydrazo-camphorate*, $\text{N}_2\text{H}_2\text{Ph} \cdot \text{CO} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Me}$, which melts at 158° and has $[\alpha]_D + 42^\circ 8'$ at 26° .

β -Methyl α -hydrogen camphorate, readily obtained by the action of alcoholic potassium hydroxide on dimethyl camphorate, yields *β -methyl camphorate α -chloride* by the action of phosphorus trichloride or thionyl chloride, from which *β -methyl- α -camphoramate* is obtained in the form of beautiful, white crystals melting at 148° , and having $[\alpha]_D + 23^\circ 20'$ at 25° .

β -Campholide, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{O}$, isomeric with *α -campholide*,

$\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ (compare Haller, *Abstr.*, 1896, i, 385; Baeyer and Villiger, *Abstr.*, 1900, i, 133; Blanc, this vol., i, 115), obtained by reducing *β -methyl α -hydrogen camphorate* with sodium in alcoholic solution, crystallises from a mixture of ether and light petroleum in white crystals melting at 218 – 220° , has $[\alpha]_D + 39^\circ 20'$ at 15° , is readily soluble in alcohol or ether, and sparingly soluble in light petroleum. The yield of *β -campholide* is very poor, and attempts to convert it into *β -camphor* through *β -cyanocampholic acid* and *β -homocamphoric acid* were unsuccessful. M. A. W.

Action of Hydroxylamine on Ethyl Acetylmalonate.

F. CARLO PALAZZO and N. SALVO (*Atti Real. Accad. Lincei*, 1905, [v], 14, ii, 252—255).—The action of hydroxylamine on ethyl acetylmalonate leads to the formation of the compound $\text{C}_7\text{H}_9\text{O}_4\text{N}$, melting at 166° and previously obtained by the action of hydroxylamine on ethyl dimethylpyronedicarboxylate (compare Palazzo, *Abstr.*, 1904, i, 762); for this compound, however, the authors suggest the constitution $\text{N}:\text{CMe} \begin{smallmatrix} \diagup \\ \text{O} - \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$ as being more probable. T. H. P.

Action of Hydroxylamine on Ethyl Diacetylmalonate.

F. CARLO PALAZZO and E. CARAPELLE (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 287—289).—The action of hydroxylamine on ethyl diacetylmalonate yields the compound $\text{C}_7\text{H}_9\text{O}_4\text{N}$ (compare preceding abstract), an acetyl group being first removed as acethydroxamic acid from the diacetyl ester by the hydroxylamine, which here acts as a hydrolyst. T. H. P.

Dihydroxyglutaric Acids. HEINRICH KILIANI and PETER

LOEFFLER (*Ber.*, 1905, 38, 3624—3626).— *$\alpha\gamma$ -Dihydroxyglutaric acid*

from *isosaccharin* (this vol., i, 739) yields a *quinine* salt, which crystallises from water in long, glistening needles. It contains $4\text{H}_2\text{O}$ and melts at 162° . The *quinine* salt of *l*-trihydroxyglutaric acid from *arabinose* contains $5\text{H}_2\text{O}$ and melts at 180° .

$\alpha\beta$ -Dihydroxyglutaric acid has been prepared by the oxidation of glutaconic acid with 1 per cent. potassium permanganate at 0° (yield 5 per cent.), and also by the action of calcium carbonate and water on glutaconic acid dibromide (yield 14 per cent.). The acid crystallises in slender needles or compact prisms, is anhydrous and optically inactive, and melts and decomposes at 164° . It can be titrated with standard alkali, yields a *quinine* salt which crystallises in large, glistening needles, and also a crystalline *potassium hydrogen* salt. The normal *sodium* and *zinc* salts have been obtained in an amorphous condition only.

An $\alpha\beta$ -dihydroxyglutaric acid has been prepared by the oxidation of *metasaccharopentose* (Abstr., 1903, i, 10) with dilute nitric acid at 35° . It crystallises in needles or plates, melts at 156° , has $[\alpha]_D + 11^\circ$, is anhydrous, and shows no tendency to lactone formation. Solutions of the alkali salts give no precipitate with barium, strontium, zinc, copper, or cadmium salts. The *potassium hydrogen* salt crystallises from aqueous alcohol in microscopic prisms. The *quinine* salt crystallises in long needles, contains $7\text{H}_2\text{O}$, and melts at $158\text{--}160^\circ$.

J. J. S.

Digitalonic Acid. HEINRICH KILIANI (*Ber.*, 1905, 38, 3621—3623). Compare Abstr., 1902, 1241).—When the lactone of digitalonic acid is oxidised with concentrated nitric acid at 35° , the chief products are oxalic and $\alpha\beta\gamma$ -trihydroxyadipic acid, $\text{C}_6\text{H}_{10}\text{O}_7$. The *calcium* salt of the latter is soluble in both hot and cold water, but is precipitated on the addition of alcohol. The *quinine* salt crystallises from water in colourless needles, contains $6\text{H}_2\text{O}$, and melts at $128\text{--}130^\circ$. The acid obtained from the *quinine* salt crystallises from water in compact plates melting at $123\text{--}124^\circ$. The *zinc* salt, $\text{C}_6\text{H}_8\text{O}_7\cdot\text{Zn}\cdot 4\text{H}_2\text{O}$, and *cupric* salt, $+4\text{H}_2\text{O}$, have been obtained in a crystalline form.

The differences between this trihydroxyadipic acid and that from *metasaccharin* (Abstr., 1885, 745) are so considerable that it is concluded that they must be structurally isomeric. The acid from digitalonic acid is thus $\alpha\beta\gamma$ -trihydroxyadipic acid,

$\text{CO}_2\text{H}[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$,
and digitalonic acid is either $\text{CH}_3\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ or
 $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{CO}_2\text{H}$.

J. J. S.

Formaldehyde. I. Formaldehyde in Aqueous Solution. FRIEDRICH AUERBACH and HERMANN BARSCHALL (*Chem. Centr.*, 1905, ii, 1081—1083; from *Arb. Kais. Ges.-A.*, 22, 584—629).—Aqueous solutions of formaldehyde are prepared by subliming trioxymethylene in a stream of nitrogen and absorbing the vapour in water. *Lumière* and *Seyewetz*' method (Abstr., 1903, i, 150) may be used for the analysis of the solutions if the correction for the hydrolysis of the sulphate solution is properly applied. *Romijn*'s method is better adapted for small quantities of dilute solutions if the following

conditions are observed. Pure alkali hydroxide, preferably prepared from the metal, should be used, the solution of iodine and alkali should not be mixed before adding the aldehyde, the addition of too much acid is to be avoided, and the liquid should be continuously shaken during the titration with sodium thiosulphate. If an insufficient quantity of iodine is used in the first instance, this cannot be remedied by adding more after the titration. The oxidation of the aldehyde appears to be entirely effected by the hypiodite formed by the action of the iodine on the alkali hydroxide. The agitation of the solution during the titration is necessary to avoid the action of the thiosulphate on the acid.

The sp. gr. of pure aqueous solutions of formaldehyde at 18° is given in the original paper, and the relationship of the average molecular weight of the aldehyde in its aqueous solution to the concentration has been determined. By means of the application of the law of mass action to the data obtained, it is shown that an equilibrium is established between the molecules of formaldehyde, CH_2O , and those of the polymeride, $(\text{CH}_2\text{O})_3$. A better agreement between the observed and calculated values is obtained, however, when it is assumed that both forms are hydrated, methylene glycol being formed from the aldehyde, CH_2O . This assumption does not preclude the possibility of the occurrence of very small quantities of higher polymerides in very concentrated solutions, and in fact the deviations shown by solutions of 37—38 volumes per cent. point to this explanation. The reaction between the two forms in aqueous solutions is reversible, and the equilibrium is attained in a short time when either gaseous formaldehyde or the polymeride is dissolved. As the temperature is raised, the latter tends to decompose into the simpler form, this change being accompanied by absorption of heat. Foelsing's (*Zeit. öffentl. Chem.*, 1904, 322) statements in reference to the effect of the preservative "sterilisol" and the difference shown by solutions prepared in a vacuum do not correspond with the facts, the composition of solutions which have been allowed to remain for a few hours being independent of the method of preparation.

When solutions of formaldehyde are distilled, the distillate is always weaker, and the residue stronger. The boiling point of aqueous solutions decreases with the concentration, and all solutions containing more than 30 vols. per cent. boil at practically the same temperature, hence on distillation a distillate of a higher boiling point is obtained (compare Konowaloff, *Abstr.*, 1881, 1093). The relationships of the composition of the vapour from boiling formaldehyde solutions to the quantity of aldehyde in the solution, and the partial pressure of the aldehyde in solutions at 100° have been determined. The partial pressure in solutions at 18° has been estimated by means of a current of air. Since these methods gave very low values, it would appear that only a very small portion of the aldehyde is contained in the solution in the form of the simple molecule CH_2O . From the partial pressures, the quantities of aldehyde which would be contained in a given volume of saturated vapour at 18° have been calculated. In the case of the strongest solution, which contained 33.8 vols. per cent., it was found that the quantity was only 0.66 gram,

and for the commercial 40 per cent. solution in methyl alcohol less than 1 gram. In practice, however, complete saturation of the vapour is never attained.

E. W. W.

Action of Ammonia and of Amines on Chloral. MITSURU KUHARA and YOSHINORI KISHI (*Mem. Coll. Sci. Eng. Kyōto*, 1904—1905, 1, 114—124).—The action of ammonia on chloral in the free state and in chloroform solution at various temperatures has been examined. The observations indicate that chloral ammonia is the first product, but that this is decomposed either (1) by rise of temperature or (2) by the action of an excess of ammonia into chloroform and formamide according to the equations: (1) $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH}_2 = \text{CHCl}_3 + \text{CHO} \cdot \text{NH}_2$; (2) $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{NH}_2 + \text{NH}_3 = \text{CHCl}_3 + \text{CH}(\text{NH}_2)_2 \cdot \text{OH} = \text{CHCl}_3 + \text{NH}_3 + \text{CHO} \cdot \text{NH}_2$. The aliphatic amines are supposed to react similarly towards chloral, and the entirely different behaviour of the aromatic amines which yield trichloroethylidene derivatives is ascribed to their much weaker basic properties. If aromatic amines are treated with chloral ammonia instead of with chloral, formyl derivatives of the amines are, however, obtained. In this reaction, the chloral ammonia first decomposes into chloroform and formamide, the latter then reacting with the amine. A number of formyl derivatives of aromatic amines were prepared according to this method.

H. M. D.

Condensation of *iso*Propylacetaldehyde [*iso*Valeraldehyde] with Acetaldehyde. BRUNO EHRENFREUND (*Monatsh.*, 1905, 26, 1003—1010).—The condensation of *isovaleraldehyde* (Rainer, this vol., i, 16) with acetaldehyde in presence of potassium carbonate has been re-investigated, as the *isovaleraldehyde* used by Wogrinz (*Abstr.*, 1901, i, 254; 1903, i, 604) contained at least *α*-methylbutaldehyde in addition.

The aldol, $\text{CH}_2\text{Pr}^\beta \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{COH}$ or $\text{OH} \cdot \text{CHMe} \cdot \text{CHPr}^\beta \cdot \text{COH}$, is now found to boil at 85° under 15 mm. pressure, and on oxidation with potassium permanganate to form, in addition to *isovaleric acid*, a *hydroxy-acid*, $\text{C}_7\text{H}_{14}\text{O}_3$.

The unsaturated aldehyde, $\text{CH}_2\text{Pr}^\beta \cdot \text{CH} : \text{CH} \cdot \text{COH}$ or $\text{CHMe} \cdot \text{CPr}^\beta \cdot \text{COH}$,

is obtained best by heating the aldol with sodium acetate; on oxidation, it yields *isovaleric acid*, *oxalic acid*, and only a small amount of *acetic acid*. Reduction of the unsaturated aldehyde with iron filings and *acetic acid* leads to the formation of a product which is probably identical with Grimshaw's *isohexylcarbinol* (this Journal, 1873, 313), and on oxidation with potassium permanganate yields *isoeptoic acid* boiling at 211—214°.

In other respects, the properties of the substances obtained agree with those described by Wogrinz (*loc. cit.*).

G. Y.

Action of Lead and Bismuth Salts on the Rotatory Power of Sugars, Polyhydric Alcohols, and Hydroxy-acids. II. HERMANN GROSSMANN (*Zeit. Ver. deut. Zucker-Ind.*, 1905, 596, 941—976. Compare this vol., i, 415).—The results of the author's

investigations on a large number of sugars, polyhydric alcohols, and hydroxy-acids show that most of these compounds readily react with alkaline solutions of lead salts, the hydrogen atoms of the hydroxyl groups being replaced by lead oxide. Owing to the change produced in the optically active molecule by the influence of the heavy lead atom, the formation of these complexes is often accompanied by a change in the sense of the rotation. The alkali necessary for the solution of the insoluble lead compounds at first produced frequently influences the rotation very greatly, especially with tartaric and quinic acids. The lead-alkali compounds of the hexoses are, in general, possessed of but little stability, the free alkali very soon producing intra-molecular changes.

A solution of bismuth nitrate in glycerol and water exerts, on addition of an alkali hydroxide, an influence on the rotation of tartaric acid, with which, together with the dextrorotatory complexes present in alkaline solution, strongly levorotatory complexes, only stable in presence of hydrogen ions, are formed. Saccharic acid is converted by alkaline bismuth solution into a strongly dextrorotatory substance.

The dextrorotation of mannitol produced by bismuth nitrate, is greater in aqueous solution than when glycerol is added. Of the sugars, only levulose and invert sugar are appreciably influenced in rotation by alkaline bismuth nitrate solution. The rotations of arabinose, galactose, dextrose, sucrose, lactose, maltose, and raffinose are diminished by alkaline bismuth nitrate solutions, but the change is here ascribed to the excess of alkali present, since increase of the amount of bismuth salt is not accompanied by a corresponding change in the rotation. The same probably holds in the case of quinic acid.

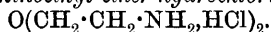
T. H. P.

Acetosulphate of Cellulose. II. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Ber.*, 1905, **38**, 3531—3538. Compare this vol., i, 512).—Particulars are given of the preparation of three series of acetylcellulose sulphuric esters and their salts, the proportions of combined sulphuric acid being 5—6, 9—10, and 25 per cent.; analyses are given of each series of compounds.

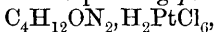
T. M. L.

Diaminoethyl Ether. SIEGMUND GABRIEL (*Ber.*, 1905, **38**, 3411—3414).—The product formerly obtained by the author (*Abstr.*, 1888, 439, 668, 1267), which Knorr (*Ber.*, 1904, **37**, 3515) has considered to be piperazine picrate, is not identical with the latter prepared directly from piperazine; the substance obtained in this way forms lemon-yellow plates and darkens between 255° and 280° without melting. The substance formerly considered to be the picrate of a base $C_4H_{12}ON_2$ is perhaps *diaminoethyl ether picrate*.

Diphthaliminoethyl ether, $(C_8H_4O_2 \cdot N \cdot CH_2 \cdot CH_2)_2O$, prepared by heating di-iodoethyl ether (Sand, *Abstr.*, 1901, i, 458 and 741) with potassium phthalimide, crystallises from alcohol in flat rhombohedra, melts at 156·5°, and when heated with hydrochloric acid and acetic acid at 140° gives *diaminoethyl ether hydrochloride*,



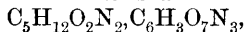
This crystallises from 96 per cent. alcohol in long, flat needles and melts at 226—227°. The corresponding *platinichloride*,



decomposes at 230°. *Diaminoethyl ether* boils at 183—184° and gives a *picrate* which decomposes at 228°. The *picrate* formerly described decomposed at 218°, so that its identity with the preceding *picrate* is not yet certain.

W. A. D.

Transformation of β -Vinylacrylic Acid into Diaminovaleric Acid. EMIL FISCHER and KARL RASKE (*Ber.*, 1905, 38, 3607—3612. Compare Fischer and Schlotterbeck, *Abstr.*, 1904, i, 549).—When heated with saturated aqueous ammonia at 150° in a closed vessel, β -vinylacrylic acid yields a *diaminovaleric acid* which, after purification by conversion into the phosphotungstate, is obtained as a dark yellow syrup. It is easily soluble in water or methyl alcohol, has a strongly alkaline reaction in aqueous solution, is precipitated by mercuric chloride, and with phosphotungstic acid forms in aqueous solution a voluminous, or in sulphuric acid solution, a granular precipitate. The diamino-acid does not yield the dibenzoyl derivative characteristic of ornithine, but it may be a mixture, possibly containing small quantities of ornithine, as it forms two crystalline *picrates*, $\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2(\text{C}_6\text{H}_3\text{O}_7\text{N}_3)_2$, which melts at 185° (corr.), and



which commences to decompose at 130°, and is melted at 160—170° (compare Schulze and Winterstein, *Abstr.*, 1902, i, 231). When distilled under reduced pressure, the diamino-acid forms an *anhydride*, $\text{C}_5\text{H}_7\text{ON}$, which crystallises in colourless, stout needles, melts at 51—53° (corr.), and is easily soluble in water, ethyl alcohol, ethyl acetate, benzene, or pyridine, and has a slight acid reaction in aqueous solution; when heated with aqueous barium hydroxide at 100°, it yields an *amino-acid*, the aqueous solution of which dissolves copper oxide. The formation of the anhydride shows that the diaminovaleric acid probably has an amino-group in the γ - or δ -position. G. Y.

Synthesis of Polypeptides. XIII. Chlorides of Amino-acids and Polypeptides, and their Use as Synthetical Agents. EMIL FISCHER (*Ber.*, 1905, 38, 2914—2925. Compare *Abstr.*, 1903, i, 465, 607, 799, 800; 1904, i, 652, 771, 867, 890, 917; this vol., i, 30, 31, 263, 637).—The author has already shown that many amino-acids, when agitated with a mixture of acetyl chloride and phosphorus pentachloride, form compounds of the type $\text{NH}_3\text{Cl}\cdot\text{CHR}\cdot\text{COCl}$. It is now shown that all simple amino-acids can be converted into the corresponding chloro-derivatives under suitable experimental conditions. The reaction has been extended to leucylglycine and to leucylglycylglycine; the resulting products combine with esters of amino-acids to form esters of higher polypeptides, which on hydrolysis are converted into the corresponding peptides. The method has been of particular advantage for the syntheses of optically active polypeptides.

Glycyl chloride hydrochloride, $\text{NH}_3\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$, is prepared as follows. Glycine is precipitated from its aqueous solution by the

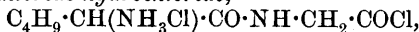
addition of a large excess of absolute alcohol, dried at 100° , and, when finely powdered, mixed with acetyl chloride. The mixture is cooled to 0° and phosphorus pentachloride gradually added, and the whole agitated for several hours. The hydrochloride is crystalline and is readily converted by ethyl alcohol into glycine ethyl ester hydrochloride.

The action of a mixture of phosphorus pentachloride and acetyl chloride on glycine which has been crystallised from water is different, other substances besides glycyl chloride hydrochloride which are not transformed by alcohol into glycine ethyl ester being formed. The author suggests the possibility of glycine existing in isomeric forms.

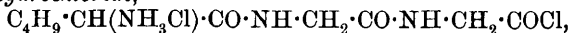
For the preparation of *d*-alanyl chloride hydrochloride, it was also found advisable to precipitate the *d*-alanine from its aqueous solution by means of absolute alcohol. *d*-Alanyl chloride hydrochloride, $\text{NH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{COCl}$, prepared by the action of a mixture of phosphorus pentachloride and acetyl chloride on *d*-alanine is a crystalline powder. The aqueous solution has $[\alpha]_D + 7.23^{\circ}$ at 20° , whilst *d*-alanine hydrochloride has $+9.55^{\circ}$. During the chlorination, racemisation to the extent of about 25 per cent. had accordingly taken place.

Phenylalanyl chloride hydrochloride, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2\text{Cl})\cdot\text{COCl}$, is a powder.

Leucylglycyl chloride hydrochloride,



prepared by the action of phosphorus pentachloride and acetyl chloride on leucylglycine, is a solid, as also is *leucylglycylglycyl chloride hydrochloride*,

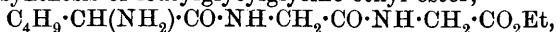


prepared from leucylglycylglycine.

Phenylalanylglycine, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by the action of phenylalanyl chloride hydrochloride on glycine ethyl ester in chloroform solution, and subsequent saponification of the resulting ester, forms colourless plates and melts and decomposes at about 273° (corr.); it is sparingly soluble in ethyl alcohol, and may also be prepared by the action of α -bromohydrocinnamyl chloride on glycine.

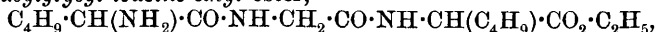
d-Alanylglycine, prepared by hydrolysis of the ester formed by the action of *d*-alanyl chloride on ethyl glycine in chloroform solution, separates from a mixture of alcohol and water in needles or in feathery crystals. It melts and decomposes at about 235° (corr.). It is the optical isomeride of the *l*-alanyl glycine, formerly described, and has $[\alpha]_D + 50.2^{\circ}$ at 20° in aqueous solution, a value slightly higher than that observed for the *l*-isomeride.

A new synthesis of leucylglycylglycine ethyl ester,



by the action of leucylglycyl chloride hydrochloride on glycine ethyl ester, is recorded.

Leucylglycyl-leucine ethyl ester,



prepared by the action of leucylglycyl chloride hydrochloride on leucine ethyl ester, is a solid, which forms a crystalline nitrate, soften-

ing at about 147° (corr.), and melting and decomposing at about 160° (corr.). The free *tripeptide* is indefinite in crystalline form, and melts and decomposes at about 253° (corr.).

A new synthesis of leucyldiglycylglycine from leucyldiglycyl chloride hydrochloride and glycine ethyl ester is recorded.

A. McK.

Complex Compounds of Organic Imides. Succinimide Copper Derivatives. LEO TSCHUGAEFF (*Ber.*, 1905, 38, 2899—2914. Compare Tschugaeff, *Abstr.*, 1904, i, 478; *Ley*, this vol., ii, 524).—The compounds of the type $(\text{Su})_2\text{Cu}, 2a$, where Su represents the succinimide group, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}$, and a the particular amine used, are prepared by four general methods. (1) The reaction, formerly employed, where cupric chloride (1 mol.) and succinimide (2 mols.) are acted on by the amine in alcoholic solution is of general applicability, but has the objection that half of the amine used is lost, since the reaction proceeds in the sense $2\text{SuH} + \text{CuCl}_2 + 4a = \text{Cu}(\text{Su})_2, 2a + 2a, \text{HCl}$. (2) When copper turnings are brought into contact with an alcoholic solution of ammonia or of a primary amine in presence of oxygen, the copper is oxidised only slowly; when, however, succinimide is added, the solution quickly becomes dark blue, and a red compound separates at once. The change is represented by the equation $4\text{SuH} + 4a + 2\text{Cu} + \text{O}_2 = 2(\text{Su})_2\text{Cu}, 2a + 2\text{H}_2\text{O}$. (3) A suitable method where the amount of amine available is small is that of warming coppersuccinimide hexahydrate with the amine in alcoholic solution. (4) A solution of cuprammine hydroxide in water or in aqueous alcohol is first prepared, and then succinimide and an excess of alcohol added, the action proceeding according to the equation $\text{Cu}(2a)(\text{OH})_2 + 2\text{SuH} = (\text{Su})_2\text{Cu}, 2a + 2\text{H}_2\text{O}$. This method, however, on account of the small yields obtained, is only of theoretical interest.

Diamminecoppersuccinimide, $(\text{Su})_2\text{Cu}, 2\text{NH}_3$, prepared by the oxidation method, begins to decompose in a closed capillary tube at 180° , and melts and decomposes at about 193° . Its aqueous solution has an ammoniacal odour; dilute solutions quickly assume a green tint and become turbid owing to hydrolysis. *Monoamine-triaquocoppersuccinimide*, $(\text{Su})_2\text{Cu}(\text{NH}_3), 3\text{H}_2\text{O}$, prepared by allowing a solution of the diammine compound in a little water to evaporate in a partial vacuum over sulphuric acid, melts at about 130° when heated in a closed capillary tube. Alcoholic ammonia converts it into the diammine compound; it may also be formed by allowing the latter to remain in the air at the ordinary temperature for some time.

Dimethylaminecoppersuccinimide, $(\text{Su})_2\text{Cu}, 2\text{NH}_2\text{Me}$, prepared by the oxidation method, separates from alcohol in red needles and melts and decomposes at 168° . Its aqueous solution is dark blue, has an odour of methylamine, and when concentrated over sulphuric acid forms the compound $(\text{Su})_2\text{Cu}(\text{NH}_2\text{Me}), 3\text{H}_2\text{O}$; the latter is bluish-violet and melts at about 118° .

Diethylamediaquocoppersuccinimide, $(\text{Su})_2\text{Cu}, 2\text{NH}_2\text{Et}, 2\text{H}_2\text{O}$, is red and melts at 156° . Its aqueous solutions undergo marked hydrolysis with the formation of coppersuccinimide hexahydrate, $(\text{Su})_2\text{Cu}, 6\text{H}_2\text{O}$; the latter forms blue plates and cannot readily be re-

crystallised from water owing to the formation of basic copper-succinimide derivatives. Coppersuccinimide hexahydrate gradually effloresces; it undergoes a delicate colour change with benzyl-, allyl-, or isobutyl-amine, a red compound being formed. Diethylamino-diaquocoppersuccinimide, in contradistinction to the corresponding ammonia and methylamine derivatives, can be preserved in a damp atmosphere without undergoing change.

The following compounds were prepared:

$(\text{Su})_2\text{Cu}, 2\text{NH}_2\text{Pr}^a$ (m. p. 167°); $(\text{Su})_2\text{Cu}, 2\text{NH}_2 \cdot \text{C}_4\text{H}_9$, *n*- (m. p. 166°); *iso*- (m. p. 171°); *sec*-; *tert*- (m. p. 161°); $(\text{Su})_2\text{Cu}, 2\text{NH}_2 \cdot \text{C}_5\text{H}_{11}$ (*iso*-) (m. p. 171°); $(\text{Su})_2\text{Cu}, 2\text{NH}_2 \cdot \text{C}_6\text{H}_{13}$ (*n*-) (m. p. 161°); $(\text{Su})_2\text{Cu}, 2\text{NH}_2 \cdot \text{C}_8\text{H}_5$ (m. p. 172°); $(\text{Su})_2\text{Cu}, 2\text{NH}_2 \cdot \text{CH}_2\text{Ph}$ (m. p. 181°); the *camphylamine* compound, $(\text{Su})_2\text{Cu}, 2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{C}_9\text{H}_{15}$.

The tendency for secondary amines to form these diammine compounds is not so marked as that of the primary amines.

Bisdimethylaminediaquocoppersuccinimide, $(\text{Su})_2\text{Cu}, 2\text{NHMe}_2, 2\text{H}_2\text{O}$, best prepared by the oxidation method, forms dark brownish-red, tetragonal prisms and melts at 133° . Its aqueous solutions are bluish-green and readily undergo hydrolytic dissociation.

Aliphatic tertiary amines do not form compounds with copper succinimide.

Dipyridinecoppersuccinimide, $(\text{Su})_2\text{Cu}, 2\text{C}_5\text{NH}_5$, forms brownish-red crystals which melt and decompose at about 175° . When its blue aqueous solution is slowly evaporated over sulphuric acid, it forms the compound $(\text{Su})_2\text{Cu}, \text{C}_5\text{NH}_5, \text{H}_2\text{O}$, which crystallises in bluish-violet needles or prisms. When the solution of the latter compound in water is allowed to evaporate over sulphuric acid or when the dipyridine compound is treated with much water and then allowed to evaporate, coppersuccinimide hexahydrate separates.

The constitution of the compounds described is discussed.

A. McK.

Selenocyanopropionic Acid. M. SIMON (*Monatsh.*, 1905, 26, 959—970. Compare Hofmann, Abstr., 1889, 726).—*Potassium α -selenocyanopropionate*, $\text{C}_4\text{H}_4\text{O}_2\text{NSeK}$, is formed by the action of potassium selenocyanate (Muthmann and Schröder, Abstr., 1900, i, 479) on potassium α -chloropropionate in slightly warm, aqueous solution; it forms deliquescent, yellow or brown crystals, and is easily soluble in alcohol or water, but almost insoluble in benzene or chloroform. The *sodium* salt, $\text{C}_4\text{H}_4\text{O}_2\text{NSeNa}$, prepared from sodium selenocyanide and α -chloropropionate, forms small, slightly yellow crystals, is readily soluble in water, but less so in alcohol, and is only slightly hygroscopic.

Sodium selenocyanate, CNSeNa , formed by fusing sodium cyanide with selenium, crystallises from alcohol in white leaflets.

Ethyl α -selenocyanopropionate, $\text{C}_6\text{H}_9\text{O}_2\text{NSe}$, formed by boiling ethyl α -chloropropionate with potassium selenocyanate in alcoholic solution in a reflux apparatus, is obtained as a reddish-brown oil, which has an unpleasant odour and a burning taste, is soluble in ether, and has a sp. gr. >1 . It is hydrolysed by boiling alcoholic sodium hydroxide with formation of sodium lactate, sodium selenocyanate and alcohol. The

methyl ester, formed by warming the potassium salt with methyl iodide, resembles the ethyl ester.

α-Selenocyanopropionic acid, $\text{CNSe} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$, liberated from its sodium salt by means of dilute sulphuric acid, forms a yellow, viscid liquid which has a characteristic odour, does not solidify at -15° , and has a strong acid reaction; when in contact with a small amount of water, it slowly evolves hydrogen cyanide, and yields on filter paper, after some time, a red selenium stain. In neutral solution, *α*-selenocyanopropionic acid forms with silver nitrate a white precipitate which becomes yellow and probably consists of a mixture of silver selenocyanate and lactate. Attempts to form a copper salt resulted also in decomposition of the acid. G. Y.

Action of Diazomethane on Ethylene and Diallyl. E. AZZARELLO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 285—286. Compare von Pechmann, *Abstr.*, 1895, i, 328).—On passing dry ethylene through a well-cooled ethereal solution of diazomethane, pyrazoline is formed.

The action of diallyl on an ethereal solution of diazomethane yields a small proportion of an oil which has an alkaline reaction, boils at $70-80^\circ$ under 28 mm. pressure, and gives a yellow precipitate with platinic chloride. T. H. P.

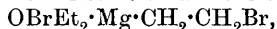
Decompositions of Ethanemercarbide with Alkali Sulphites and Sulphur Chloride. KARL A. HOFMANN and H. FEIGEL (*Ber.*, 1905, 38, 3654—3659. Compare *Abstr.*, 1898, i, 635; 1900, i, 383).—When the chloride, $\text{C}_2\text{Hg}_6\text{Cl}_6$, is shaken with ten times its weight of a 10 per cent. benzene solution of sulphur chloride, no change occurs; it is also undecomposed when heated with sulphur chloride at 120° . The corresponding base, $\text{C}_2\text{Hg}_6\text{O}_4\text{H}_2$, on the other hand, when shaken with the benzene solution, yields yellow crystals of the compound $\text{C}_2\text{Hg}_4\text{Cl}_4\text{S}_2$, probably $\begin{array}{c} \text{C}(\text{HgCl})_2 \cdot \text{C}(\text{HgCl})_2 \\ \text{S} \text{-----} \text{S} \end{array}$, the chlorine of which is readily precipitated as silver chloride.

When the chloride, $\text{C}_2\text{Hg}_6\text{Cl}_6$, is mixed with potassium polysulphide solution and the solution repeatedly renewed so long as mercuric chloride is formed, the compound $\text{C}_2\text{Hg}_4\text{Cl}_2\text{SH}_2$ is obtained in the form of brilliant yellow needles. The same product is obtained when the mixture is heated at 100° and is purified by washing with potassium sulphide solution, water, alcohol, carbon disulphide, and ether. When the yellow crystals are boiled with hydrochloric acid, an intense alliaceous odour is noticed, and a white, crystalline powder is formed which turns yellow on the addition of hot sodium hydroxide solution. The chlorine atoms are removed by silver nitrate and are thus presumably attached to mercury, and the formula $\begin{array}{c} \text{ClHg} \cdot \text{CH} \cdot \text{Hg} \\ \text{ClHg} \cdot \text{CH} \cdot \text{Hg} \end{array} > \text{S}$ is suggested.

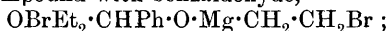
The base $\text{C}_2\text{Hg}_6\text{O}_4\text{H}_2$, when left for several weeks in contact with a methyl-alcoholic solution of ammonium polysulphide, which is repeatedly renewed, yields a yellow compound, which, after washing with potassium sulphide solution, has the composition $\text{C}_2\text{Hg}_6\text{S}_2\text{O}_2\text{H}_2$.

It has not been found possible to remove all the metal from these mercury compounds by means of sulphides and polysulphides. Tetramercuriethane cyanide reacts with potassium polysulphide yielding the compound, $C_4Hg_4SH_6$, probably $(Hg:CH \cdot CH_2 \cdot Hg)_2S$. With a methyl-alcoholic solution of ammonium polysulphide, it yields $C_2Hg_2SH_4$. J. J. S.

Grignard's Reaction with Dihaloids. II. FELIX B. AHRENS and ADOLF STAPLER (*Ber.*, 1905, 38, 3259—3267. Compare this vol., i, 423).—The compound formed by the action of magnesium on ethylene dibromide in ethereal solution has the constitution

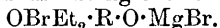


and its additive compound with benzaldehyde,



when treated with water under cooling, this is decomposed with formation of ether and benzaldehyde. The *additive* compound with *p*-tolualdehyde, $OBrEt_2 \cdot CH(C_7H_7) \cdot O \cdot Mg \cdot CH_2 \cdot CH_2Br$, is obtained as a white powder melting at 117° . The *additive* compound with piperonal, $OBrEt_2 \cdot CH(C_6H_3 \cdot O_2 \cdot CH_2) \cdot O \cdot Mg \cdot CH_2 \cdot CH_2Br$, melts at 210° .

The action of anhydrous bromine on magnesium in cooled ethereal solution leads to the formation of the *additive* compound, $OBrEt_2 \cdot MgBr$, which is obtained as an unstable oil; in ethereal solution, it forms the following additive compounds having the constitution



With benzaldehyde, $R = CHPh$, a white, crystalline powder which melts partially at 164 — 165° ; with *p*-tolualdehyde, $R = CH \cdot C_7H_7$: a white powder which commences to sinter at 105 — 107° and melts at 120 — 122° ; with furfuraldehyde, $R = CH \cdot C_4H_3O$: a brown compound which commences to sinter and decompose at 164° ; with ethyl acetoacetate, $R = C(OEt) \cdot CH_2 \cdot COMe$: white leaflets, melting at 146 — 148° ; with ethyl malonate, $R = C(OEt) \cdot CH_2 \cdot CO_2Et$: a white powder which sinters at 124° and melts at 128 — 129° ; with 2:6-dimethylpyridine, $R = NC_5H_3Me_2$: a white compound which commences to soften at 161° , and melts slowly at 168 — 230° ; with piperidine, $R = NC_5H_{11}$: a yellowish-white substance which does not melt at 270° ; with *p*-toluidine, $R = NH_2 \cdot C_7H_7$: a white substance which sinters and blackens at 225° ; with acetone, a deliquescent, yellow mass.

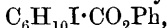
The action of iodine on magnesium in ethereal solution leads to the formation of the unstable *additive* compound, $OIEt_2 \cdot MgI$; this is obtained as a viscid oil which slowly deposits crystals of magnesium iodide.

The action of bromine on calcium in cooled ethereal solution leads to the formation of the *additive* compound, $OBrEt_2 \cdot CaBr$, which is obtained as a yellowish-brown, crystalline mass containing unchanged calcium particles; it forms with piperidine in ethereal solution a white, powdery *additive* derivative. G. Y.

Modern Position of the Benzene Theory. HUGO KAUFFMANN (*Chem. Centr.*, 1905, ii, 965; from *Chem. Zeitschr.*, 4, 289—290).—The paper contains a description of the principles on which research on the constitution of benzene has been developed in recent times.

E. W. W.

Derivatives of cycloHexane. LÉON BRUNEL (*Ann. Chim. Phys.*, 1905, [viii], 6, 200—288).—The present paper is mainly a *résumé* of work already published (compare Abstr., 1903, i, 157, 338, 680, 695; this vol., i, 123, 268, 274, 340), and contains in addition a description of the following new compounds: *o*-Iodocyclohexyl benzoate,



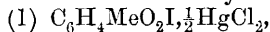
crystallises from a mixture of alcohol and ether in large, colourless plates melting at 54° . *o*-Bromiodocyclohexane, $\text{C}_6\text{H}_{10}\text{BrI}$, a pale red oil with an odour similar to that of camphor, is insoluble in water, soluble in alcohol, ether, or acetic acid, has a sp. gr. 2.07 at 0° , and boils at $134\text{--}136^\circ$ under 28 mm. pressure (compare Abstr., 1903, i, 157). *o*-Ethylaminocyclohexanol, $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{NHEt}$, crystallises in small, colourless, hygroscopic needles which become coloured by the action of light, melt at $44\text{--}45^\circ$, and boil at 222° under atmospheric pressure; its *hydrochloride* forms colourless, deliquescent plates melting at 155° . *Ethyl dihydroxycyclohexylamine*, $\text{NEt}(\text{C}_6\text{H}_{10}\cdot\text{OH})_2$, crystallises in small, colourless, odourless plates melting at 114° , and boiling at 352° ; its *hydrochloride* forms colourless crystals melting at $162\text{--}163^\circ$. *o*-Diethylaminocyclohexanol, $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{NEt}_2$, is a colourless oil boiling at 230° and forming a crystalline *hydrochloride* melting at 168° . *o*-Phenylaminocyclohexanol, $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{NHPh}$, is a colourless, crystalline substance melting at 58° , boiling at 210° under 46 mm. or 327° under atmospheric pressure; its *hydrochloride* melts at $150\text{--}151^\circ$. *o*-Phenylmethylaminocyclohexanol, $\text{OH}\cdot\text{C}_6\text{H}_{10}\cdot\text{NMePh}$, is a colourless oil boiling at 192° under 28—30 mm., or 202° under 40 mm., or at 329° under 767 mm. pressure (compare Abstr., 1903, i, 680). *Methoxy- Δ^2 -cyclohexene*, $\text{C}_6\text{H}_9\cdot\text{OMe}$, a colourless mobile oil with a strong alliaceous odour, boils at 139.8° and has a sp. gr. 0.928 at 0° ; *ethoxy- Δ^2 -cyclohexene*, $\text{C}_6\text{H}_9\cdot\text{OEt}$, a colourless, mobile oil boiling at 154.5° and having a sp. gr. 0.911 at 0° (compare Crossley, *Trans.*, 1904, 85, 1415—1416); the *cyclohexenol*, $\text{C}_6\text{H}_9\cdot\text{OH}$, obtained from either of the two preceding compounds, is a liquid boiling at $164\text{--}166^\circ$ and reacting with phenylcarbimide to form the urethane, $\text{C}_6\text{H}_9\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, melting at 108° .

M. A. W.

Double Salts of Iodoxy-derivatives with Mercuric Chloride and Bromide. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 199—205).—The double salts here described may be prepared by the following methods: (1) by adding mercuric chloride or bromide to a hot aqueous solution of the iodoxy-compound; (2) by treating phenyl iododichloride with mercuric chloride in aqueous solution; (3) in the case of iodoxybenzene, by passing a current of dry chlorine into a solution of iodobenzene in glacial acetic acid containing yellow mercuric oxide. These double salts all crystallise well and are more stable towards the action of heat than the iodoxy-derivatives they contain.

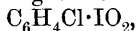
The following compounds have been prepared: $\text{C}_6\text{H}_5\text{O}_2\text{I}\cdot\text{HgCl}_2$, which crystallises from water in white needles, decomposing without deflagrating at $225\text{--}227^\circ$; $\text{C}_6\text{H}_5\text{O}_2\text{I}\cdot\text{HgBr}_2$, which separates from water in radiating masses of white needles, beginning to colour at about 260° , and becoming quite yellow at 305° . *p*-Iodoxytoluene

yields : (1) $C_6H_4MeO_2I, HgCl_2$, which crystallises from water in thin, plate-like masses of white needles, decomposing at $214-215^\circ$ when rapidly heated, and (2) a *mercuribromide*, forming silky, mammillary masses of slender, white needles, which blacken at about 290° . *m*-Iodoxytoluene gives : (1) $C_6H_4MeO_2I, HgCl_2$, which separates in radiating white prisms, turning yellow at about 200° and decomposing at 260° ; (2) a *mercuribromide*, which crystallises in slender needles beginning to turn yellow at 240° . *o*-Iodoxytoluene forms :



which separates in stellar aggregates of white needles, blackening at 190° and decomposing rapidly at 210° ; (2) $C_6H_4MeO_2I, \frac{1}{2}HgBr_2$, which forms flocculent masses of slender prisms turning yellow at 240° .

The following iodoxy-derivatives have been prepared : β -iodoxy-naphthalene, $C_{10}H_7IO_2$, exploding at 200° ; *p*-chloriodoxybenzene,



exploding at 232° ; *p*-bromiodoxybenzene, $C_6H_4Br \cdot IO_2$, exploding at 231° , and *p*-nitroiodoxybenzene, $NO_2 \cdot C_6H_4 \cdot IO_2$, exploding at 216° . Unsuccessful attempts have been made to prepare double salts of mercuric haloids with these compounds, some of the latter being insoluble in water and other solvents, whilst others crystallise unchanged in presence of mercuric salts.

p-Nitrotoluene forms the double salt, $NO_2 \cdot C_6H_4Me, HgCl_2$, separating from alcohol in pale yellow, acicular crystals, which soften at about 105° , begin to melt at 150° , and blacken at about 222° .

T. H. P.

Action of Alkyl Haloids on the Sodium Derivatives of Arylsulphoneacetonitriles. JULIUS TRÖGER and PAUL VASTERLING (*J. pr. Chem.*, 1905, [ii], 72, 323—340. Compare Tröger and Hille, this vol., i, 336; Tröger and Volkmer, this vol., i, 356).—Arylsulphonedialkylacetonitriles are prepared by heating the disodium derivatives, formed by the action of sodium ethoxide in absolute alcoholic solution on arylsulphonacetonitriles, with methyl iodide, ethyl or propyl bromides, or benzyl chloride in sealed tubes or in a reflux apparatus on the water-bath. They are more stable than the parent substances, hydrolysis, as also formation of amidoximes, taking place only with difficulty or not at all.

Benzenesulphonedithylacetonitrile, $SO_2Ph \cdot CEt_2 \cdot CN$, crystallises from alcohol in colourless, rhombic plates and melts at 78° . *Benzenesulphonedibenzylacetonitrile*, $SO_2Ph \cdot C(C_6H_5)_2 \cdot CN$, crystallises from alcohol in long, glistening, sparingly soluble needles and melts at $157-157.5^\circ$. *Benzenesulphonedüisopropylacetonitrile* is obtained as a viscid, brown oil.

p-Chlorobenzenesulphonedithylacetonitrile, $C_6H_4Cl \cdot SO_2 \cdot CEt_2 \cdot CN$, separates from alcohol in small crystals and melts at 81° . *p*-Chlorobenzenesulphonedipropylacetonitrile and *p*-chlorobenzenesulphonedüisopropylacetonitrile are obtained as oils. *p*-Chlorobenzenesulphonedibenzylacetonitrile crystallises from hot alcohol and melts at 125° .

p-Bromobenzenesulphonedithylacetonitrile separates from alcohol in small, white, rhombic crystals and melts at 94° . *p*-Bromobenzene-

sulphonedibenzylacetoneitrile crystallises from alcohol in white needles and melts at 145° .

p-Iodobenzenesulphonedibenzylacetoneitrile crystallises from alcohol in small needles or glistening spangles and melts at 166° .

α -*Naphthalenesulphonedimethylacetoneitrile* crystallises from alcohol in white spangles and melts at 115° . α -*Naphthalenesulphonedibenzylacetoneitrile* separates from alcohol in small, white, rhombic crystals and melts at 180° .

β -*Naphthalenesulphonedimethylacetoneitrile* crystallises from alcohol in glistening, white spangles and melts at 115° .

β -*Naphthalenesulphonedimethylacetoneitrile* is obtained as a viscid, brown oil. β -*Naphthalenesulphonedibenzylacetoneitrile* crystallises in small, white, sparingly soluble needles and melts at 177° .

The action of 1 mol. of benzyl chloride on the monosodium derivative of β -naphthalenesulphoneacetoneitrile leads to the formation of the dibenzyl derivative, together with a *substance* which crystallises in light, white needles, melts at 128° , and may be the monobenzyl-derivative.

ψ -*Cumylsulphonedimethylacetoneitrile* is obtained as an oil.

p-*Phenetolesulphondimethylacetoneitrile* separates from alcohol in small, white, rhombic crystals and melts at 81° . *p*-*Phenetolesulphonedibenzylacetoneitrile* crystallises in small, white needles and melts at 119° .

o-*Anisolesulphonedimethylacetoneitrile* is obtained as an oil. *o*-*Anisolesulphonedibenzylacetoneitrile* forms small, rhombic crystals and melts at 123° .

p-*Anisolesulphonedibenzylacetoneitrile* separates from alcohol in small, rhombic crystals and melts at 119° .

Sodio-p-chlorobenzenesulphoneacetoneitrile, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\cdot\text{CHNa}\cdot\text{CN}$, is obtained as a hygroscopic, dirty-white powder when the nitrile is treated with 1 mol. of sodium ethoxide in alcoholic solution and the product precipitated by ether; when warmed with 1 mol. of benzyl chloride in ethereal alcoholic solution, it yields a small amount of a crystalline *product* melting at 117° . The *monosodium* derivative of *p*-bromobenzenesulphoneacetoneitrile, obtained in the same manner, forms a hygroscopic, yellowish-white powder, and when heated with 1 mol. of benzyl chloride in ethereal alcoholic solution yields a *substance* which forms small, yellow crystals and melts at 104° .

Whilst benzenesulphoneacetoneitrile and α -naphthalenesulphoneacetoneitrile are hydrolysed by hydrogen chloride in glacial acetic acid solution in a sealed tube on the water-bath, with formation of benzenesulphonic acid and α -naphthalenesulphonic acid respectively, and *p*-bromobenzenesulphoneacetoneitrile is hydrolysed to the acid by prolonged heating with aqueous sodium hydroxide, β -naphthalenesulphonedimethylacetoneitrile is hydrolysed only partially by concentrated sulphuric acid in a sealed tube at 120 – 150° for one day, or by prolonged heating with 15 per cent. alcoholic potassium hydroxide, with formation of a small amount of β -naphthalenesulphonedimethylacetic acid, which was identified by means of its barium salt.

Benzenesulphonedipropylthioacetamide, $\text{SO}_2\text{Ph}\cdot\text{CPr}_2\cdot\text{CS}\cdot\text{NH}_2$, is formed when the nitrile is heated with alcoholic ammonium sulphide

in a sealed tube in the water-bath; it is obtained as a yellow, voluminous substance.

p-Anisolesulphonedibenzylthioacetamide, formed in the same manner, is obtained in small, yellowish-white, loose crystals and melts at 114°. G. Y.

p-Dichloroaminobenzene [2:5-Dichloroaniline]. EMILIO NOELTING and ÉMILE KOPP (*Ber.*, 1905, 38, 3506—3515).—2:5-Dichloroaniline melts at 50° and boils at 246° (corr.) at 744 mm. pressure; it is a weak base, the salts of which can be crystallised from alcohol, but are decomposed by water. The *hydrochloride* forms colourless needles and melts at 191—192°; the *sulphate*, glistening scales melting at 196—197°; the *nitrate*, scales which char at 165°, liberating brown vapour. The *benzoyl* derivative crystallises from alcohol in silky needles and melts at 120°. The *thiocarbamide*, $\text{CS}(\text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2)_2$, prepared with some difficulty, crystallises from alcohol in very slender, colourless needles and melts at 174°; it yields a thiocarbimide when heated with strong mineral acids.

When diazotised, 2:5-dichloroaniline shows a great tendency to form a diazoamino-compound, and to prevent this it is necessary to use at least 7—8 mols. of acid; the best method is to diazotise in concentrated sulphuric acid. The *diazoperbromide*, $\text{C}_6\text{H}_3\text{Cl}_2\text{N}_2\text{Br}_3$, precipitated by ether from a solution in acetone, forms small, yellow plates and melts and decomposes at 160°. 2:5-Dichlorobenzeneazo- β -naphthol, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, separates from acetic acid in slender, orange-red needles and melts at 184°; condensation products were also obtained with salicylic acid, β -naphtholdisulphonic acids R and G, and aminonaphtholdisulphonic acid H.

2:5-Dichlorobenzonitrile, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{CN}$, forms colourless, silky needles, melts at 130°, sublimes when cautiously heated, and is saponified by heating with fuming hydrochloric acid at 180°.

1:4-Dichloro-2-bromobenzene forms glistening, white needles and melts at 35°.

2:5-Dichlorophenol forms a colourless, radially-crystalline mass, melts at 58°, and boils at 211° under 744 mm. pressure.

2:5-Dichlorophenylhydrazine, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{N}_2\text{H}_3$, crystallises in slender, white needles from hot water, in which it is fairly soluble, melts at 105°, becomes yellow on exposure to the air, and reduces cold Fehling's solution. The hydrochloride crystallises from dilute hydrochloric acid in white needles. The *p*-nitrobenzylidene derivative,

$\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, crystallises in orange-coloured needles and melts at 220°. The *p*-dimethylaminobenzylidene derivative forms yellow, stout crystals and melts at 120°. The *osazone* with dihydroxytartaric acid is readily prepared, and passes, when heated on the water-bath, into the *pyrazolone*, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{N} \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2 \\ \text{N} = \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$, which crystallises (unacetylated) from acetic anhydride in slender, orange-coloured needles and melts and decomposes at 236°.

The *sodium nitrosoamino*-compound (*isodiazotate*), $\text{C}_6\text{H}_3\text{Cl}_2\text{N}_2\text{ONa}$,

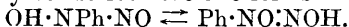
separates from alcohol in long, yellow crystals and yields a sparingly soluble white isodiazohydroxide.

The *monosulphonic acid*, $C_6H_2Cl_2(NH_2) \cdot SO_3H$ [2 : 5 : 4 : 1], separates from hot water in anhydrous, white, glistening needles. The *sodium* salt separates in white, glistening plates with $5H_2O$, and the *barium* salt is anhydrous. The acid is oxidised by chromic acid to 2 : 5-dichloroquinone, and is converted by bromine into 2 : 5-dichloro-4 : 6-dibromoaniline, $C_6HCl_2Br_2 \cdot NH_2$, which is insoluble in water and in dilute mineral acids, separates from 50 per cent. acetic acid in white needles, and melts at 108° . The sulphonic acid yields a stable *diazonium-anhydride* which separates in glistening, white needles. 2 : 5-Dichlorophenylhydrazinesulphonic acid, $C_6H_2Cl_2(N_2H_3) \cdot SO_3H$, forms anhydrous, slender, white needles and yields a canary-yellow tartrazine; the *sodium* salt separates with $3\frac{1}{2}H_2O$ in white scales with a fatty lustre.

The *diacetyl* derivative of dichloro-*p*-phenylenediamine melts at $294-296^\circ$. The *o*-diamine sublimes in glistening, white needles, which melt at 100° and do not become coloured when kept; *phenanthra-dichlorophenazine*, $C_6H_2Cl_2 \begin{smallmatrix} N:C \cdot C_6H_4 \\ | \quad | \\ N:C \cdot C_6H_4 \end{smallmatrix}$, forms soft, yellow needles and melts at 289° .

T. M. L.

Nitration of Amines. ANGELO ANGELI and GIUSEPPE MARAGLIANO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 127—132).—The water which is eliminated in the reaction between a nitric ester and hydroxylamine is formed from an oxygen atom of the nitro-group and the hydrogen of the amino-residue. This is shown by the fact that the reaction takes place even in absence of the hydroxyl of the hydroxylamine. Thus, the addition of sodium to an absolute ethereal solution of molecular proportions of aniline and acetyl nitrate leads to the formation of the sodium salt of phenylnitroamic acid, $NPh \cdot NO \cdot OH$, which represents the tautomeric form of phenylnitroamine, $NHPh \cdot NO_2$. The latter is isomeric with nitrosophenylhydroxylamine, to which may be ascribed the two forms



Hence, although nitrosophenylhydroxylamine can be obtained by the action (1) of hydroxylamine on nitrobenzene, (2) of hyponitrous acid on nitrosobenzene, or (3) of nitrous acid on phenylhydroxylamine, it is impossible to prepare it by the interaction of nitric acid and aniline.

T. H. P.

Action of Magnesium Alkyl Haloids on Amines and on Ammonium, Amine, and Hydrazine Salts, and a New Method of Formation of Hydrocarbons. JOSEF HOUBEN (*Ber.*, 1905, 38, 3017—3021. Compare *Abstr.*, 1904, i, 1014; Sachs and Sachs, *Abstr.*, 1904, i, 925).—The action of 1 mol. of aniline on 2 mols. of magnesium methyl iodide in ethereal solution cooled by ice leads to the formation of the additive compound, $NHPh \cdot MgI, MgMeI$, which does not absorb carbon dioxide, but reacts with 1 mol. of aniline to form methane and the compound $NHPh \cdot MgI$; this forms an *additive compound*, $NHPh \cdot CO_2 \cdot MgI$, with carbon dioxide in ethereal solution cooled with ice.

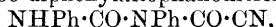
Ammonium chloride, bromide, iodide, carbonate, sulphate, nitrate, persulphate and chromate, phenylhydrazine hydrochloride, and aniline hydrochloride and nitrate are decomposed by magnesium methyl iodide, with formation of methane and in most cases of a heavy, colourless oil, insoluble in ether; the similar reaction takes place more violently with magnesium ethyl chloride or bromide; magnesium phenyl bromide and magnesium benzyl chloride are decomposed by ammonium chloride. At higher temperatures, as, for example, in boiling anisole solution, a second hydrogen atom of the ammonium, amine, or hydrazine salt is substituted, and a smaller quantity of the salt is therefore required for the decomposition of the same amount of the magnesium alkyl haloid. G. Y.

Behaviour of Hydrogen Cyanide towards Phenylcarbimide.

WALTER DIECKMANN and HEINRICH KÄMMERER (*Ber.*, 1905, **38**, 2977—2986. Compare Dieckmann, Hoppe, and Stein, this vol., i, 135).—Hydrogen cyanide and phenylcarbimide interact only in the presence of alkaline substances, such as potassium cyanide, sodium carbonate, sodium acetate, or pyridine. *Cyanoformanilide*, $\text{NHPh}\cdot\text{CO}\cdot\text{CN}$, is formed by adding a few drops of pyridine to a solution of hydrogen cyanide and phenylcarbimide in benzene; it crystallises from benzene in glistening, colourless leaflets or from aqueous alcohol or acetic acid in fan-like aggregates of broad needles, melts and decomposes into its generators at about 120° , is readily soluble in alcohol, ether, chloroform, or carbon disulphide, but less so in benzene or glacial acetic acid, and is only sparingly soluble in light petroleum or water. It gives a violet-red coloration with potassium dichromate in concentrated sulphuric acid solution. By prolonged contact with water or aqueous solvents, more quickly when warmed, it is decomposed with formation of hydrogen cyanide and diphenylcarbamide, and when boiled with alcohol for twelve hours, it yields hydrogen cyanide and ethyl phenylcarbamate. The alkaline solution of cyanoformanilide deposits diphenylcarbamide slowly at the ordinary temperature, more quickly when heated, the solution containing the alkali cyanide together with small amounts of oxanilic acid; in alcoholic potassium hydroxide or sodium ethoxide, ethyl phenylcarbamate appears instead of the diphenylcarbamide. With aqueous ammonia, it forms phenylcarbamide, with aniline, diphenylcarbamide, and with phenylhydrazine, diphenylsemicarbazide.

The action of cyanoformanilide on ethyl sodioacetoacetate leads to the formation of ethyl acetomalonanilate, melting at 57° . Phenyl-oxamide is formed by the action of hydrogen chloride on cyanoformanilide in glacial acetic acid solution cooled by ice, or by the action of hydrogen peroxide on cyanoformanilide in presence of an alkali hydroxide. With hydrogen sulphide in alcoholic solution, cyanoformanilide yields phenylthionoxamide melting at 176° (Reissert, *Abstr.*, 1904, i, 991).

In aqueous solution, in presence of traces of an alkali hydroxide, potassium cyanide, sodium carbonate or acetate, or pyridine, hydrogen cyanide and phenylcarbimide interact with development of heat to form a *product*, which may be diphenylallophanonitrile,



or diphenylparabanimide, $\text{CO} \begin{smallmatrix} \text{NPh} \cdot \text{CO} \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$; it crystallises from alcohol in white needles, melts at 137° , is easily soluble in glacial acetic acid, but only sparingly so in cold alcohol, ether, benzene, or carbon disulphide, and is almost insoluble in water. It dissolves in dilute alkali hydroxides, and is gradually decomposed into diphenylcarbamide, oxanilic acid, and a small quantity of alkali cyanide; with alcoholic alkali hydroxides, ethyl phenylcarbamate is formed, whilst with ammonia, aniline, and phenylhydrazine it yields phenylcarbamide, diphenylcarbamide, and diphenylsemicarbazide respectively. When treated with acids, it yields diphenylparabanic acid. G. Y.

Action of Phosphorus Pentachloride on Tartranil. SADAJIRO OKADA (*Mem. Coll. Sci. Eng. Kyōto*, 1904—1905, 1, 168—171).—Dichloromaleinanil and 2:3:4:5-tetrachloro-1-phenylpyrrole are formed when *d*-tartranil is treated with phosphorus pentachloride. Dichlorosuccinanil is assumed to be the first product in the formation of dichloromaleinanil, but it immediately loses 1 mol. of hydrogen chloride with the formation of monochloromaleinanil, in which one atom of hydrogen is then replaced by chlorine. H. M. D.

Simple Preparation of Pure Ethylaniline from Commercial Ethylaniline. G. BLUME and H. KLÖFFLER (*Ber.*, 1905, 38, 3276).—Pure ethylaniline hydrochloride is obtained in a yield of 80 per cent. of the theoretical by adding 65 c.c. of concentrated hydrochloric acid to 97 grams of commercial ethylaniline, and completing the precipitation by passing a current of hydrogen chloride through the filtrate. G. Y.

Optically Active α -Phenylethylamines (α -Aminoethylbenzenes). JOHAN M. LOVÉN (*J. pr. Chem.*, 1905, [ii], 72, 307—314. Compare Abstr., 1897, i, 37; Pope and Harvey, *Trans.*, 1899, 75, 1110; Kipping and Hunter, *Trans.*, 1903, 83, 1147; Marckwald and Meth, this vol., i, 272).—When α -phenylethylamine and *l*-malic acid are stirred together with water, solution takes place with development of heat, and α -phenylethylamine *l*-malate separates as a crystalline powder; this crystallises in large, three-sided prisms, is soluble in 18.1 parts of water at 10° , and yields the *d*-base having $[\alpha]_D + 40.27^\circ$ at 15° . *l*- α -Phenylethylamine *l*-malate is highly soluble in water, crystallising only from a viscid syrup.

The base obtained from the filtrate from the *l*-malate of the *d*-base yields, when treated with *d*-tartaric acid in a small quantity of water, *l*- α -phenylethylamine hydrogen *d*-tartrate, which crystallises in hemimorphic, monoclinic, short prisms or stout plates, or, on rapid cooling of the hot saturated aqueous solution, in slender needles containing water of crystallisation; the hydrated form changes into the stable, anhydrous modification when warmed or on addition of a trace of the prismatic crystals. The *l*-base has $[\alpha]_D - 39.72^\circ$ at 6° ; its *carbamide*, crystallises in matted, slender needles and has $[\alpha]_D - 43.6^\circ$ with a concentration of 0.1406 gram/c.c., or -52.1° with a concentration of

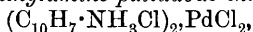
0.03717 gram/c.c. ; the *nitrate*, $\text{CHMePh} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2, \text{HNO}_3$, crystallises in glistening plates. G. Y.

Palladium. ALEXANDER GUTBIER [with A. KRELL and R. L. JANSSEN] (*Zeit. anorg. Chem.*, 1905, 47, 23—41).—In former papers (this vol., ii, 584), the preparation of double salts and palladosammine derivatives by interaction of palladous chloride and bromide with the hydrochlorides and hydrobromides of aniline and *o*- and *p*-toluidine has been described. Corresponding compounds of xylydine, *p*-anisidine, and α - and β -naphthylamine have now been prepared by the methods previously given. Whereas the double salts can be readily crystallised from dilute hydrochloric and hydrobromic acids respectively, the palladosammine derivatives are extremely insoluble, and so far no satisfactory solvent has been found for the naphthylamine and benzidine compounds. The xylydine and *p*-anisidine derivatives can be crystallised from a large excess of alcohol.

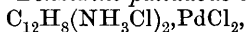
The phenylenediamines react differently from the other bases, since salts of the meta- and para-compounds yield double salts with the palladous salts under all conditions, whereas the ortho-compounds yield only platosammine derivatives. The latter are so stable that they can be recrystallised from the corresponding dilute halogen acids.

All the palladosammine compounds here described are acted on by warm concentrated ammonia, the base being set free and a pallado-diammine chloride or bromide, $[\text{Pd}(\text{NH}_3)_4\text{Cl}_2]$, formed. On heating, the base is driven off and finally the diammine loses two molecules of ammonia, palladosammine chloride or bromide remaining in solution.

Xylydine palladous chloride, $(\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH}_3\text{Cl})_2, \text{PdCl}_2$, is obtained in clear, brown needles; the *bromide* forms reddish-brown leaflets. *p*-*Anisidine palladous chloride*, $[\text{C}_6\text{H}_4(\text{OMe}) \cdot \text{NH}_3\text{Cl}]_2, \text{PdCl}_2$, crystallises in yellowish-brown leaflets; the *bromide* also forms lustrous, yellowish-brown leaflets. *α -Naphthylamine palladous chloride*,



occurs in glistening, yellowish-brown leaflets, the *bromide* in dark brownish-red needles. The *chloride* of the β -compound forms yellowish-red leaflets; the corresponding *bromide* crystallises in dark reddish-brown leaflets. *Benzidine palladous chloride*,

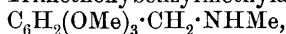


crystallises in brown leaflets, the *bromide* in small, reddish-brown leaflets. *m*-*Phenylenediamine palladous chloride*, $\text{C}_6\text{H}_4(\text{NH}_3\text{Cl})_2, \text{PdCl}_2$, crystallises in glancing copper-coloured leaflets, the corresponding para-compound in small, reddish-brown leaflets; its *bromide* also occurs in reddish-brown leaflets.

Dixylylpalladosammine chloride, $\text{Pd}(\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH}_2)_2\text{Cl}_2$, crystallises from hot alcohol in small, golden-yellow needles; the *bromide* separates in small, glistening, golden-yellow needles. *Di-p-anisidylpalladosammine chloride*, $\text{Pd}[\text{C}_6\text{H}_4(\text{OMe})\text{NH}_2]_2\text{Cl}_2$, and the corresponding *bromide* both crystallise from hot alcohol in small, yellow needles. *Di- α -naphthylpalladosammine chloride* and *bromide* and the corresponding β -compounds are all obtained as very slightly soluble, yellow powders. *Benzidylpalladosammine chloride*, $\text{Pd}[\text{C}_6\text{H}_4 \cdot \text{NH}_2]_2\text{Cl}_2$,

cannot easily be obtained pure on account of the great difficulty of separating it from the slightly soluble benzidine hydrochloride; it forms a yellow precipitate. The *bromide* is also very difficult to purify; it forms a yellowish-brown precipitate. *o*-Phenylene palladosammine chloride, $\text{Pd}[\text{C}_6\text{H}_4(\text{NH}_2)_2]\text{Cl}_2$, crystallises from dilute hydrochloric acid in small, greenish-yellow, shining needles; the *bromide* separates from dilute hydrobromic acid in golden-brown, glancing needles. G. S.

Attempts to Synthesise Mezcaline. ARTHUR HEFFTER and R. CAPELLMANN (*Ber.*, 1905, **38**, 3634—3640. Compare *Abstr.*, 1901, i, 737).—3 : 4 : 5-Trimethoxybenzylmethylamine,

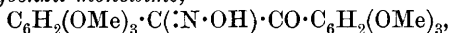


has been synthesised, and it is shown that it is not identical, but isomeric with mezcaline.

Gallonitrile trimethyl ether, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CN}$, may be obtained by Krüss' method (*Abstr.*, 1884, 1314) by heating gallic acid trimethyl ether with lead thiocyanate. It crystallises from dilute alcohol in needles, melts at 95° , and dissolves readily in alcohol or ether, but only sparingly in hot water. Its solution in concentrated sulphuric acid has a yellowish-red colour. When reduced with sodium by Ladenburg's method, it yields a considerable amount of the corresponding acid and hydrogen cyanide, but very little primary amine.

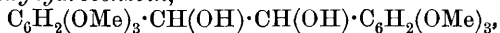
Gallaldehyde trimethyl ether, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CHO}$, may be prepared by the oxidation of the corresponding alcohol (*Abstr.*, 1891, 1218) by the action of potassium cyanide in a mixture of alcohol and sodium carbonate on hexamethoxybenzil or by the oxidation of hexamethoxyhydrobenzoin with potassium dichromate and acetic acid.

Hexamethoxybenzil monoxime,



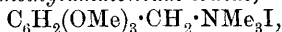
exists in two modifications. The α -compound, which is insoluble in benzene, crystallises from dilute alcohol in long needles melting at 158° . The β -derivative is soluble in benzene, crystallises from dilute alcohol in slender, felted needles, and melts at 138° .

Hexamethoxyhydrobenzoin,



obtained as a by-product in the reduction of gallamide trimethyl ether, crystallises from alcohol in well-developed needles melting at 215° . Its solution in concentrated sulphuric acid has a yellow colour. The *diacetate* melts at 190° .

Gallaldehyde trimethyl ether, purified by means of its bisulphite compound, crystallises from dilute alcohol in glistening plates, melts at 77° , and is readily soluble in alcohol or ether. The *oxime* crystallises in long needles, melts at 91° , and yields a crystalline *hydrochloride*. When reduced with sodium amalgam and alcohol, the oxime yields 3 : 4 : 5-trimethoxybenzylamine, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CH}_2\cdot\text{NH}_2$, in the form of a yellow oil with pronounced alkaline properties and is readily soluble in water, alcohol, or ether. The *sulphate*, $(\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}_2)_2\cdot\text{H}_2\text{SO}_4\cdot 3\text{H}_2\text{O}$, crystallises from water in absolute glistening needles and is insoluble in alcohol. The *platinichloride* crystallises in yellow needles and melts at 197° .

Trimethoxybenzyltrimethylammonium iodide,

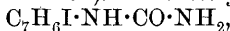
crystallises from water in stout plates melting at 218° and readily soluble in water or alcohol. The *platinichloride* melts at 215° and is sparingly soluble in water. This quaternary ammonium iodide is not identical, but isomeric with methylmezcaline methiodide. J. J. S.

Resolution of Phenylbenzylmethylpropylammonium Bases into their Optical Antipodes. EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1905, **38**, 3438—3446).—*Phenylbenzylmethylpropylammonium iodide*, prepared either from methylpropylaniline and benzyl iodide or from benzylmethylaniline and propyl iodide, crystallises in colourless, flat, six-sided plates, which become yellow at 140° and melt and decompose at 147° . *Phenylbenzylmethylpropylammonium bromide*, prepared from methylpropylaniline and benzyl bromide, crystallises in colourless prisms and decomposes at 173 — 174° . Benzyl chloride and methylpropylaniline do not interact. *Phenylbenzylmethylpropylammonium d-camphorsulphonate* crystallises in rhombic plates, often a centimetre long, and melts at 179° ; when fractionally crystallised from methyl formate, a fraction was obtained, the base from which gave $[\alpha]_D + 13.28^\circ$ and $[M]_D + 62.55^\circ$, and, converted into the corresponding iodide, had $[\alpha]_D + 3.21^\circ$ and $[M]_D + 11.8^\circ$.

l-Phenylbenzylmethylpropylammonium d-bromocamphorsulphonate, prepared by the interaction of the ammonium bromide with the sulphonic acid, yields a first fraction, about half the theoretical amount, having $[\alpha]_D + 4.83^\circ$ and $[M]_D + 26.59^\circ$. After two crystallisations from a mixture of ethyl acetate and alcohol, it shows $[\alpha]_D - 2.67^\circ$ and $[M]_D - 14.67^\circ$. The corresponding *l-phenylbenzylmethylpropylammonium iodide* has in alcoholic solution $[\alpha]_D - 96.47^\circ$ and $[M]_D - 354^\circ$, and in chloroform solution $[\alpha]_D - 102^\circ$ and $[M]_D - 374^\circ$. The chloroform solution showed autoracemisation, the rotation falling in one case in four hours to $[M]_D - 178^\circ$, whilst next day the solution was optically inactive. The *l*-iodide decomposes at 149 — 150° .

The *d-phenylbenzylmethylpropylammonium iodide*, obtained from the mother liquors of the bromocamphorsulphonate, has $[\alpha]_D + 86.74^\circ$, $[M]_D + 319^\circ$. E. F. A.

Introduction of Iodine into Tolylocarbamides. PAUL ARTMANN (*Monatsh.*, 1905, **26**, 1091—1108).—*5-Iodotolyl-2-carbamide*,



is formed by the action of potassium iodide and iodate on *o*-tolylcarbamide in boiling aqueous solution and treatment of the solution with hydrochloric acid, or by heating *o*-tolylcarbamide with iodine and mercuric oxide in alcoholic solution at 70 — 75° , or by treating 5-iodo-2-aminotoluene with potassium cyanate in cold glacial acetic acid solution. It crystallises from aqueous alcohol in long, white, hair-like needles, is easily soluble in alcohol, pyridine, or glacial acetic acid, less so in boiling water, and is insoluble in ether, benzene, or light petroleum; when boiled with acetic anhydride in a reflux apparatus, it is decomposed with formation of 5-iodo-2-acetotoluidide. The *acetyl* derivative, $\text{C}_{10}\text{H}_8\text{O}_2\text{N}_2\text{I}$, is formed by dropping acetyl chloride

into the pyridine solution of 5-iodotolyl-2-carbamide at 0° ; it crystallises in small, white prisms and melts at $234\text{--}235^{\circ}$. 6-Iodo-*tolyl-3-carbamide* can be prepared from *m*-tolylcarbamide or from 6-iodo-3-aminotoluene by the same three methods as 5-iodotolyl-2-carbamide. It crystallises in short, white needles, melts at 187° , and when boiled with acetic anhydride forms 6-iodo-3-acetotoluidide. The *acetyl* derivative, formed by the action of acetyl chloride on 6-iodotolyl-3-carbamide in pyridine solution, crystallises in sheaves of slender, white needles and melts at $170\text{--}171^{\circ}$. 3-Iodo-6-nitrotoluene, $\text{C}_7\text{H}_6\text{O}_2\text{NI}$, is formed by the action of potassium iodide on diazotised 6-nitro-3-aminotoluene; it crystallises in slender, orange needles, melts at 84° , is volatile in a current of steam, and is reduced by ferrous sulphate and ammonia in aqueous solution at $66\text{--}70^{\circ}$ to 5-iodo-2-aminotoluene, $\text{C}_7\text{H}_5\text{NI}$. This crystallises in long, white needles, melts at $91\text{--}92^{\circ}$, and is easily soluble in alcohol, ether, glacial acetic acid, benzene, light petroleum, or hot water. The salts are hydrolysed by water and decompose slowly on exposure to the air; the *hydrochloride*, $\text{C}_7\text{H}_5\text{NI}\cdot\text{HCl}$, forms short, white needles; the *nitrate*, $\text{C}_7\text{H}_5\text{NI}\cdot\text{HNO}_3$, crystallises in slender, tetragonal scales. 5-Iodo-2-acetotoluidide, $\text{C}_9\text{H}_{10}\text{ONI}$, formed by the action of acetic anhydride on 5-iodo-2-aminotoluene in ethereal solution, crystallises from alcohol in matted, slender needles and melts at $161\text{--}162^{\circ}$.

6-Iodo-3-aminotoluene, formed by reduction of 6-iodo-3-nitrotoluene, crystallises in colourless leaflets, melts at $98\text{--}99^{\circ}$, and decomposes slowly on exposure to air. The *hydrochloride* forms short needles, the *nitrate* crystallises in tree-like aggregates of slender needles. 6-Iodo-3-acetotoluidide, formed by boiling 6-iodo-3-toluidine with acetic anhydride, crystallises in white needles and melts at 132° . G. Y.

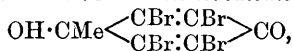
Action of Nitric Acid on the Halogen Derivatives of *p*-Alkylphenols. II. Action of Nitric Acid on the Bromo-derivatives of *p*-Cresol. THEODOR ZINCKE (*Annalen*, 1905, 341, 309—354).—[With WILHELM EMMERICH.]—5-Bromo-3-nitro-*p*-cresol, $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{BrMe}\cdot\text{OH}$, is prepared by the action of nitric acid on bromo-*p*-cresol in acetic acid solution, or by the action of nitrous acid on an acetic acid solution of either monobromo- or dibromo-*p*-cresol, and crystallises in yellow needles melting at 68° . It dissolves in dilute sodium carbonate solution with a red coloration, and is oxidised by nitric acid to bromonitro-*p*-toluquinone. 5:6-Dibromo-3-nitro-*p*-cresol (?), prepared by the action of nitrous acid on an acetic acid solution of tribromo-*p*-cresol, crystallises in yellow, shining needles or leaflets melting at 124° and yields a red sodium salt. When heated with nitric acid, dibromonitro-*p*-toluquinone is formed. 2:5:6-Tribromo-3-nitro-*p*-cresol is prepared in a similar manner from tetrabromo-*p*-cresol, or more easily from tetrabromoquinnitrole, and crystallises in pale yellow needles melting at 160° ; the *sodium* salt is intensely red. Bromonitro-*p*-toluquinone, $\text{CO}\langle\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{NO}_2) \\ \text{CMe}=\text{CBr} \end{smallmatrix}\rangle\text{CO}$ or $\text{CO}\langle\begin{smallmatrix} \text{CMe}\cdot\text{C}(\text{NO}_2) \\ \text{CH}=\text{CBr} \end{smallmatrix}\rangle\text{CO}$, prepared from monobromo-*p*-cresol or bromonitro-*p*-cresol by oxidation with nitric acid, crystallises in golden needles or six-sided plates,

melting at 135—136°, and yields a derivative with aniline which crystallises in brownish-red leaflets, decomposing at 220—230°. *Bromonitro-p-toluquinol*, prepared by reducing the quinone with hydriodic acid in acetic acid solution, crystallises in long, yellow needles melting at 175—176°; its salts are of a dark red colour, but its *diacetyl* derivative, $\text{NO}_2 \cdot \text{C}_6\text{HBrMe}(\text{OAc})_2$, crystallises in colourless prisms melting at 118°. *5-Bromo-3-amino-p-toluquinol*, prepared by reduction of the bromonitrotoluquinone with tin and hydrochloric acid, crystallises in needles which melt and decompose at 148—149°; it is readily oxidised in alkaline solution, and forms a hydrochloride which crystallises in colourless needles; it is oxidised by ferric chloride to a compound, $\text{C}_7\text{H}_6\text{O}_2\text{NBr}$, probably an iminoquinone, which crystallises in black needles, dissolves in sulphuric acid with a blue coloration, and is decomposed with evolution of ammonia by alkali hydroxides. The *triacetyl* derivative of the bromoaminotoluquinol, $\text{NHAc} \cdot \text{C}_6\text{HBrMe}(\text{OAc})_2$, crystallises in needles melting at 203—204°.

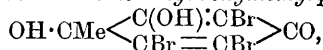
Dibromonitro-p-toluquinone, $\text{CO} \begin{smallmatrix} \text{CBr}=\text{CBr} \\ \text{CMe}:\text{C}(\text{NO}_2) \end{smallmatrix} \text{CO}$, prepared by the oxidation of nitrodibromo-*p*-cresol, crystallises in golden leaflets melting at 165° and decomposing at 175—180°; it is reduced by hydriodic acid in acetic acid to a *quinol* which crystallises in needles melting at 157—158°.

[With M. BUFF.]—Di-, tri-, and tetra-bromo-*p*-cresols are very readily converted into quinnitroles, which in their turn yield ψ -quinols. On reduction, both quinnitroles and ψ -quinols yield the same phenols. In many respects the bromoquinnitroles behave differently to the chloroquinnitroles. The ψ -quinols react with Grignard's reagent, yielding di- ψ -quinols, which are converted by sulphuric acid into hydrocarbons having a quinonoid structure.

2:3:5:6-*Tetrabromomethylquinnitrole*, $\text{NO}_2 \cdot \text{CMe} \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \text{CO}$, prepared by the action of concentrated nitric acid on tetrabromo-*p*-cresol in acetic acid solution, crystallises in white plates melting and decomposing at 100°; it passes easily into the corresponding ψ -quinol, and when heated with alcoholic hydrochloric acid yields 2:5:6-tri-bromo-3-nitro-*p*-cresol. 2:3:5:6-*Tetrabromomethyl- ψ -quinol*,

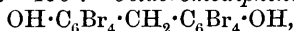


prepared either from the corresponding quinnitrole or by the action of nitric acid on tetrabromo-*p*-cresol, crystallises in monoclinic plates melting at 205°; its *acetyl* derivative forms colourless needles melting at 175—176°. 2:3:5-*Tribromo-6-hydroxymethylquinol*,



prepared by the action of 10 per cent. sodium hydroxide on the corresponding ψ -quinol, crystallises with H_2O in monoclinic plates which melt and decompose at 131°, and when anhydrous melt at 152°. Its *monoacetyl* derivative crystallises in needles melting at 179°. Tetra-bromo- ψ -toluquinol yields an *anilide*, $\text{OH} \cdot \text{CMe} \begin{smallmatrix} \text{C}(\text{NHPh}):\text{CBr} \\ \text{CBr}=\text{CBr} \end{smallmatrix} \text{CO}$, which crystallises in yellow needles melting at 206°; its *acetyl*

derivative forms greenish-yellow needles which are sensitive to light and decompose at 170—190°. *Octabromodiphenolmethane*,



prepared by warming the ψ -quinol with concentrated sulphuric acid, crystallises in white needles, melting and decomposing at 280—281°. When the quinol and bromine are heated under pressure at 100°, *tetrabromo-p-cresol ψ -bromide* is formed.

3:6-Dichloro-2:5-dibromomethyl- ψ -quinol, $\text{C}_6\text{Br}_2\text{Cl}_2\text{OMe(OH)}$, prepared by heating tetrabromotolu- ψ -quinol with alcoholic hydrochloric acid under pressure at 100°, crystallises in white plates or prisms melting at 172°, and is soluble in alkali hydroxides. Its *acetyl* derivative crystallises in needles melting at 147°. It reacts with aniline with elimination of hydrogen chloride and the formation of an *anilide*, $\text{C}_{13}\text{H}_{10}\text{O}_2\text{NClBr}_2$, which crystallises in yellow needles melting at 197°.

3:6-Dichloro-5-bromo-2-hydroxy- ψ -toluquinol, $\text{C}_7\text{H}_5\text{O}_3\text{Cl}_2\text{Br} \cdot 2\text{H}_2\text{O}$, prepared by the action of 10 per cent. sodium hydroxide on dichloro-dibromo- ψ -quinol, crystallises in colourless plates melting at 174—175°; dibromodichloro- ψ -quinol is reduced by stannous chloride in acetic acid solution to *3:6-dichloro-2:5-dibromo-p-cresol*, which crystallises in long needles melting at 175—176°; its *acetyl* derivative crystallises in needles melting at 146—147°. When heated with excess of bromine under pressure at 100°, it is converted into *3:6-dichloro-2:5-dibromo-p-cresol- ψ -bromide*, which forms colourless needles melting at 166°. Boiling water converts the ψ -bromide into a *hydroxybenzyl alcohol*, which crystallises in needles melting and decomposing at 175°; the corresponding *methoxy-derivative*, $\text{OMe} \cdot \text{C}_6\text{Cl}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OH}$, is obtained when the ψ -bromide is boiled with methyl alcohol, and crystallises in plates melting at 155°. *3:6-Dichloro-2:5-dibromotoluquinnitrole*, $\text{C}_7\text{H}_5\text{O}_3\text{NCl}_2\text{Br}_2$, is prepared by the action of nitric acid on dichloro-dibromo-*p-cresol*, and crystallises in needles melting and decomposing at 83—85°; when boiled with methyl alcohol, it yields the methoxy-derivative just mentioned.

2:3:5-Tribromoquinnitrole, $\text{NO}_2 \cdot \text{CMe} \begin{matrix} \text{CH} \cdot \text{CBr} \\ \text{CBr} \cdot \text{CBr} \end{matrix} \text{CO}$, prepared by

the action of nitric acid on tribromo-*p-cresol*, could not be prepared in a pure state, but the corresponding *2:3:5-tribromomethyl- ψ -quinol* is obtained when the tribromo-*p-cresol* is treated with nitric acid in acetic acid solution; it forms plate-like crystals melting at 128°; its *acetyl* derivative crystallises in plates melting at 127—128°. On reduction with stannous chloride, the tribromo-*p-cresol* is regenerated; when heated with sulphuric acid, the ψ -quinol yields *hexabromodiphenolmethane*, which crystallises in needles melting at 202—203°.

Chlorodibromomethyl- ψ -quinol is prepared from dichlorodibromotoluquinol and crystallises in prisms melting at 134—135°; its *acetyl* derivative crystallises in needles melting at 117°. On reduction, the ψ -quinol yields *chlorodibromo-p-cresol*, which crystallises in needles melting at 65°; its *acetyl* derivative melts at 76°.

Dibromo-*p-cresol* yields with nitric acid *2:6-dibromomethylquinnitrole*, crystallising in needles melting and decomposing at 62° (compare Auwers, *Abstr.*, 1902, i, 217). It is converted into dibromomethyl- ψ -quinol,

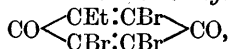
$\text{OH} \cdot \text{CMe} \langle \begin{smallmatrix} \text{CH}:\text{CBr} \\ \text{CH}:\text{CBr} \end{smallmatrix} \rangle \text{CO}$, when suspended in a solution of nitric acid in acetic acid; it crystallises in needles melting at $134\text{--}135^\circ$. When treated with concentrated sulphuric acid, it forms *tetrabromodiphenol-methane*, $\text{CH}_2(\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2$, melting at 227° .

Tetrabromomethylethyl-di- ψ -quinol, $\text{OH} \cdot \text{CMe} \langle \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \rangle \text{CEt} \cdot \text{OH}$, prepared after Grignard's method from tetrabromomethyl- ψ -quinol by treatment with magnesium foil and ethyl iodide in ethereal solution, crystallises in white needles melting at $190\text{--}191^\circ$ and soluble in alkali hydroxides; when heated with hydrogen bromide in acetic acid solution, it yields the compound $\text{C}_9\text{H}_7\text{Br}_5$, which crystallises in needles melting at $169\text{--}170^\circ$ and is insoluble in alkali hydroxides. *Tetrabromodiethyl- ψ -quinol*, $\text{OH} \cdot \text{CEt} \langle \begin{smallmatrix} \text{CBr}:\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \rangle \text{CEt} \cdot \text{OH}$, prepared in a similar manner from tetrabromoethylquinol, crystallises in plates melting at $179\text{--}180^\circ$, and is converted by hydrogen bromide in acetic acid solution into a compound (possibly *tetrabromo-p-diethylbenzene*), melting at $112\text{--}114^\circ$. *Dichlorodibromomethylethyl-di- ψ -quinol*, $\text{C}_9\text{H}_{10}\text{O}_2\text{Cl}_2\text{Br}_2$, is prepared in similar manner and crystallises in needles melting at 183° .
K. J. P. O.

Action of Nitric Acid on Tri- and Tetra-bromo-*p*-ethylphenols. THEODOR ZINCKE and HANS REINBACH (*Annalen*, 1905, 341, 355—364).—The bromo-derivatives of *p*-ethylphenol resemble those of *p*-cresol in their behaviour towards nitric acid; quinnitroles have not, however, been obtained, although they are probably formed as intermediate products; the ψ -quinols were isolated.

2:5-Dibromo-3-nitro-p-ethylphenol, $\text{C}_6\text{HBr}_2\text{Et}(\text{OH})\cdot\text{NO}_2$, prepared from *2:3:5-tribromo-p-ethylphenol* by the action of nitric acid or sodium nitrite on its acetic acid solution, crystallises in yellow needles melting at $105\text{--}106^\circ$ and forms a red sodium salt. The *acetyl* derivative crystallises in pale yellow prisms melting at 60° . *Tribromo-nitro-p-ethylphenol*, prepared in a similar manner from tetrabromo-*p*-ethylphenol, crystallises in yellow needles melting at $122\text{--}123^\circ$; its *acetyl* derivative forms yellow plates melting at 113° .

2:3:5-Tribromoethyl- ψ -quinol, $\text{OH} \cdot \text{CEt} \langle \begin{smallmatrix} \text{CH}=\text{CBr} \\ \text{CBr}:\text{CBr} \end{smallmatrix} \rangle \text{CO}$, prepared by prolonged treatment of tribromo-*p*-ethylphenol with nitric acid in acetic acid solution, crystallises in needles melting at 105° and soluble in alkali hydroxide; it yields an *acetyl* derivative and regenerates the phenol on reduction. *2:3:5:6-Tetrabromoethyl- ψ -quinol*, prepared from tetrabromoethylphenol by boiling with nitric acid containing nitrous acid, crystallises in needles melting at $139\text{--}140^\circ$. Its *acetyl* derivative forms crystals melting at 124° . *Tribromoethyl-p-quinone*,



prepared by the action of concentrated sulphuric acid on finely-powdered tetrabromo- ψ -quinol, crystallises in yellow leaflets or needles melting at $118\text{--}120^\circ$. With aniline, it gives an *anilide*, $\text{O}:\text{C}_6\text{Br}_2\text{Et}(\text{NHPh})\cdot\text{O}$, crystallising in dark violet needles melting

and decomposing at 167—170°. *Tribromoethylquinol*, $C_6Br_3Et(OH)_2$, prepared by reducing the quinone with stannous chloride, crystallises in needles melting at 141°. Its *diacetyl* derivative crystallises in prisms or plates melting at 156—157°. K. J. P. O.

Some Phenolic Ethers containing the ψ -Allyl Chain $R \cdot CMc \cdot CH_2$. AUGUSTE BÉHAL and MARC Tiffeneau (*Compt. rend.*, 1905, 141, 596—597. Compare Abstr., 1904, i, 742).—Phenolic ethers containing the ψ -allyl chain are completely hydrogenated by the action of sodium and absolute alcohol, forming the corresponding *iso*-propyl compound; *o*-, *m*-, and *p*-*isopropylanisoles*, boiling respectively at 194—196°, 205—208°, and 210—212°, were thus prepared from the corresponding ψ -propenylanisoles. *p*-*iso*Propylphenetole, boiling at 220° and having a sp. gr. 0.946 at 0°, was prepared in similar manner from ψ -propenylphenetole; 1-*iso*propyl-3:4-veratrole, boiling at 232—236°, from 1- ψ -propenyl-3:4-veratrole, and 1-*iso*-propyl-3:4-catechol methylene ether, boiling at 230—233°, from 1- ψ -propenyl-3:4-catechol methylene ether (compare Delange, Abstr., 1904, i, 741). By the action of potassium permanganate, the ψ -allyl compounds are oxidised, yielding derivatives of acetophenone; *o*-methoxyacetophenone, boiling at 245°, *m*-methoxyacetophenone, boiling at 132° under 15 mm. pressure, and *p*-methoxyacetophenone, melting at 38°, were obtained from the three corresponding ψ -propenylanisoles, 3:4-dimethoxyacetophenone, melting at 48°, from 1- ψ -propenyl-3:4-veratrole, and 3:4-methylenedioxyacetophenone, melting at 88°, from 1- ψ -propenyl-3:4-catechol methylene ether. The iodohydrins of the ψ -allyl compounds suffer an intermolecular rearrangement under the action of silver nitrate or mercuric oxide (compare Abstr., 1901, i, 272; 1902, i, 666), whereby *p*- ψ -propenylanisole is converted into *p*-methoxybenzyl methyl ketone (compare Tardy, Abstr., 1903, i, 46), *p*- ψ -propenylphenetole into *p*-ethoxybenzyl methyl ketone, 1- ψ -propenyl-3:4-catechol methylene ether into methylene-3:4-dioxyacetophenone, and 1- ψ -propenyl-3:4-veratrole into 3:4-dimethoxybenzyl methyl ketone (compare Wallach, Abstr., 1904, i, 753, and Höring, this vol., i, 593). By the action of potassium hydroxide, the iodohydrins of the ψ -allyl compounds are converted into the corresponding substituted ethylene oxide, which on distillation yields the corresponding hydratropaldehyde (compare this vol., i, 523, 591; Bougault, Abstr., 1902, i, 452). M. A. W.

Phenols Insoluble in Aqueous Alkali Hydroxides. MOISSEI ROGOFF (*J. pr. Chem.*, 1905, [ii], 72, 315—322. Compare Abstr., 1901, i, 152; Fosse, Abstr., 1902, i, 304; 1903, i, 510; 1904, i, 83, 336, 337; Fosse and Robyn, this vol., i, 607).—A *résumé* is given of the phenols which have been described as insoluble in aqueous alkali hydroxides. The author agrees with Fosse and Robyn (*loc. cit.*) that the insolubility of the dinaphthaxanthyl phenols is due to the quadri-valency of the oxygen atom, a view which is supported by the isolation of xanthoxonium salts (Werner, Abstr., 1902, i, 50). The insolubility of the phenols of the acridine series is due similarly to the quinquivalent nitrogen atom.

The condensation products of aldehydes with β -naphthylamine and

with β -naphthol, described in the present paper, are insoluble in cold, and only sparingly soluble in warm, dilute alkali hydroxides.

The *product* obtained on heating 1 mol. of *p*-hydroxybenzaldehyde with 2 mols. of β -naphthylamine in alcoholic hydrochloric acid solution in a sealed tube at 150—155° crystallises from dilute acetic acid in matted needles, melts at 249—251° (corr.), and is easily soluble in methyl or ethyl alcohol or acetone, forming solutions with bluish-violet fluorescence. The *benzoate* crystallises in needles and melts at 268·5—269·5° (corr.); the *acetate* crystallises from hot dilute alcohol and melts at 204—207° (corr.).

The *condensation product* from vanillin and β -naphthylamine crystallises from chloroform in slender needles, melts at 254—256° (corr.), forms solutions with slight bluish-violet fluorescence in methyl or ethyl alcohol, ether, acetone, or benzene, and is soluble in aqueous-alcoholic sodium hydroxide.

p-Hydroxyphenylnaphthaxanthen (Fosse, Abstr., 1904, i, 83) is formed when *p*-hydroxybenzaldehyde is heated with β -naphthol in glacial acetic acid solution in a sealed tube at 190—200°; it melts at 203—205° (corr.) (207°, Fosse). The *acetyl* derivative melts at 190—192·5° (corr.); the *benzoyl* derivative crystallises in needles and melts at 273·5—274·5° (corr.). When condensed in presence of hydrogen chloride in glacial acetic acid solution, *p*-hydroxybenzaldehyde and β -naphthol form *p*-hydroxyphenylnaphthaxanthen, together with a substance which crystallises from alcohol, melts at 267·5° (corr.), is insoluble in aqueous alkali hydroxides, but dissolves in aqueous-alcoholic sodium hydroxide, and when warmed with sulphuric acid has a green fluorescence.

The condensation of *m*-hydroxybenzaldehyde and β -naphthol in glacial acetic acid solution at 190—200° leads to the formation of a compound which crystallises from dilute methyl alcohol in needles, melts at 249—251° (corr.), is almost insoluble in boiling aqueous alkali hydroxides, and dissolves in warm concentrated sulphuric acid to form a solution which has a green fluorescence. G. Y.

Oxidation of $\beta\beta$ -Dinaphthol. HANS BÜNZLY and HERMAN DECKER (*Ber.*, 1905, 38, 3268—3273).—When oxidised with potassium ferricyanide in alkaline solution, $\beta\beta$ -dinaphthol yields (a) *o*- β -hydroxynaphthoylbenzoic acid (Walder, Abstr., 1883, 666), which crystallises from boiling glacial acetic acid in matted, colourless scales, melts at 255°, and sublimes, forming yellow drops of oil; these crystallise on cooling in yellow needles melting at 145—150°; (b) a neutral substance, $C_{20}H_{12}O_3$, which remains after removal of the acid from the oxidation product; it crystallises from carbon disulphide in dark brown needles, melts at 230°, is sparingly soluble in glacial acetic acid, alcohol, or ether, and dissolves in concentrated sulphuric acid to form a green solution which has a blue fluorescence and becomes blue when heated. When heated, it evolves vapours with a quinone-like odour, and forms a small quantity of a substance, which may be

dinaphthylene dioxide, $\text{CH} \begin{array}{c} \diagup \text{CH} - \text{C} \begin{array}{c} \diagup \text{O} \cdot \text{C} \begin{array}{c} \diagup \text{CH} \cdot \text{CH} \end{array} \diagdown \text{CH} \\ \diagdown \text{C} = \text{C} \begin{array}{c} \diagup \text{C} = \text{C} \end{array} \diagdown \text{C} - \text{CH} \end{array} \end{array} \diagdown \text{CH} \end{array}$; it sublimes

in long, slender, golden needles, melts at 245° , is only sparingly soluble in organic solvents, forming solutions with dark blue fluorescence, and dissolves in concentrated sulphuric acid to form a red solution, which becomes violet-red and finally blue on dilution with water. On reduction with hydriodic acid and phosphorus under pressure, it yields a small quantity of partially reduced naphthalene derivative, and when distilled with zinc dust it is converted to a small extent into naphthalene.

The *picrate* crystallises in large, black needles and decomposes into its generators when treated with solvents. The *tetranitro*-derivative, $C_{20}H_6O_{10}N_4$, is formed by the action of nitric acid of sp. gr. 1.5 on the dioxide; on addition of alcohol to its solution in nitrobenzene, it separates as a cinnabar-like, crystalline meal, does not melt at 300° , is sparingly soluble in most organic solvents, but somewhat more soluble in glacial acetic acid or nitrobenzene, and forms a light red solution in concentrated sulphuric acid.

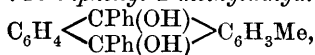
The action of methyl sulphate on 2:7-dihydroxynaphthalene in aqueous sodium hydroxide solution leads to the formation of the mono- and di-methyl ethers. 7-Hydroxy-2-methoxynaphthalene, $C_{11}H_{10}O_2$, crystallises from water in white scales, or from alcohol in long needles, melts at $113-114^{\circ}$, is soluble in aqueous alkali hydroxides, sublimes without decomposition, is volatile in a current of steam, has only a slight fruity odour, and dissolves in concentrated sulphuric acid to form a dark yellow solution with bluish-green fluorescence, from which it is precipitated unchanged on dilution with water. 2:7-Dihydroxynaphthalene and its mono- and di-methyl ethers give with aqueous ferric chloride white or yellow precipitates which rapidly become black.

G. Y.

Dinaphthylene Oxides. OSKAR ECKSTEIN (*Ber.*, 1905, **38**, 3660—3663).—The dinaphthylene oxides obtained by heating β -naphthol with litharge (Knecht and Unzeitig, *Abstr.*, 1881, 281) and by heating β -dinaphthol with zinc chloride or phosphorus pentachloride (*Ber.*, 1882, **15**, 2171) are shown to be identical and to have the constitution 1:1'-dinaphthyl 2:2' oxide. Both melt at 158.5° (corr.) and both yield a monopicate melting at $163-163.5^{\circ}$ (corr.) and a dipicate melting at 168.5° .

J. J. S.

γ -Substituted Anthracene Derivatives. ALFRED GUYOT and CH. STAHLING (*Bull. Soc. chim.*, 1905, [iii], **33**, 1104—1121. Compare Haller and Guyot, *Abstr.*, 1904, i, 314, 659, and this vol., i, 188).—9:10-Dihydroxy-9:10-diphenyl-2-methyldihydroanthracene,



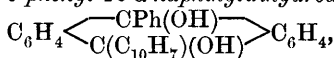
prepared by the action of magnesium phenyl bromide on 2-methyl-anthraquinone, forms small, colourless, apparently cubical crystals, melts at 240° , and is difficultly soluble in organic solvents, but dissolves in sulphuric acid forming an indigo-blue solution. The *dichloride*, obtained by the action of hydrogen chloride on the parent substance dissolved in benzene, forms colourless leaflets, melts at 148° ,

and at the same time evolves hydrogen chloride; the latter is also produced when the dichloride is dissolved in sulphuric acid, an indigo-blue solution being formed. The *dimethyl ether*, formed in the usual manner, crystallises from its solution in benzene on addition of methyl alcohol and melts at 169° ; the *diethyl ether*, similarly prepared, forms small, brilliant white crystals and melts at 183.5° .

9:10-Dihydroxy-9:10-diphenyl-2-methyldihydroanthracene, in presence of acids, as an oxidising agent and yields, under these conditions, 9:10-*diphenyl-2-methylanthracene*, which separates from benzene on addition of alcohol in greenish-yellow crystals, melts at 213° , and is slightly soluble in alcohol, ether, or acetic acid, but readily so in benzene or its homologues. The solutions show a fine bluish-violet fluorescence (compare Abstr., 1904, i, 314). On reduction by means of sodium amalgam in alcohol, this hydrocarbon is converted into the corresponding *dihydride*, which crystallises from acetic acid in colourless, silky needles, melts at 179° , and is soluble in most organic solvents. On exposure to air, the dihydride slowly acquires a greenish tint due to superficial oxidation to the parent hydrocarbon, and, like the latter, on oxidation with potassium dichromate yields the original 9:10-dihydroxy-9:10-diphenyl-2-methyldihydroanthracene. The latter readily condenses with various aromatic compounds to yield complex derivatives: thus, with dimethylaniline, it furnishes 9:10-*tetramethyldiaminodiphenyl-9:10-diphenyl-2-methyldihydroanthracene*, $C_6H_4 \left\langle \begin{array}{c} CPh \cdot C_6H_4(NMe_2) \\ CPh \cdot C_6H_4(NMe_2) \end{array} \right\rangle C_6H_3Me$. This exists in two forms (*cis* and *trans*), both being colourless, crystalline powders: one melts at 312° and is slightly soluble in most organic solvents, the other melts at about 147° and is readily soluble. Both forms yield crystalline *picrates* and *platinichlorides* and *salts*, which are dissociated by water. These substances give no coloration when dissolved in sulphuric acid. When the condensation is carried out at 100° , only one of the hydroxyl groups is replaced by the dimethylaniline residue. The *product* appears to be a mixture of at least two isomerides and, on adding hydrochloric acid to its solution in alcohol, two substances are obtained, one melting at 155° and the other at 125° . These may be isomerides or may be related to each other as hydroxy-compound and ethyl ether.

9:10-*Dihydroxy-9:10- α -dinaphthylidihydroanthracene*, prepared by the action of magnesium α -naphthyl bromide on anthraquinone, forms small, colourless crystals containing 1 mol. of benzene, and is soluble in acetic acid, ether, or boiling toluene, but scarcely so in other solvents. When dissolved in boiling benzene and treated with hydrogen chloride, the corresponding dichloride is probably first formed, but this, under the conditions of the experiment, loses 1 mol. of hydrogen chloride and yields a *monochloro*-derivative, which forms greenish-yellow crystals, melts at 266° , and is readily soluble. The position of the chlorine atom in this substance is not known.

When reduced by zinc and acetic acid, the dihydroxy-compound yields 9:10-*di- α -naphthylanthracene*; this forms small, pale yellow crystals, and dissolves in benzene or its homologues with a pronounced violet fluorescence.

9:10-Dihydroxy-9-phenyl-10- α -naphthylidihydroanthracene,

prepared by the action of magnesium naphthyl bromide on phenyl-oxanthranol, separates from solutions in benzene in small, apparently cubical crystals, melts at 220° , and has properties similar to those of the other dihydroxy-compounds of this type. The corresponding *dichloride* crystallises from benzene in small, colourless prisms containing 1 mol. of the solvent, which is rapidly lost at 15° ; the effloresced product melts at 160° . The *dimethyl ether* forms small, brilliant crystals and melts at 230° ; the *diethyl ether* resembles it and melts at 239° .

9-Phenyl-10- α -naphthylanthracene, prepared by reducing the parent substance with zinc and acetic acid, forms yellow, microscopic crystals, melts at about 229° , and is readily soluble in benzene and its homologues, much less so in alcohol or acetic acid; the solutions show a bluish-violet fluorescence. This substance, on reduction with sodium amalgam in alcohol, furnishes 9-phenyl-10- α -naphthylidihydroanthracene. This crystallises in colourless needles, but assumes a violet tint, on exposure to air, due to superficial oxidation and melts at about 225° .

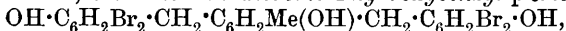
9:10-Tetramethyldi-*p*-aminodiphenyl-9-phenyl-10- α -naphthylidihydroanthracene, produced by condensing dimethylaniline with dihydroxy-phenylnaphthylidihydroanthracene dissolved in acetic acid, is a colourless, crystalline powder, melts at about 260° , and gives no coloration with sulphuric acid.

T. A. H.

Condensation of ψ -Phenols with Phenols. KARL AUWERS and E. RIETZ (*Ber.*, 1905, 38, 3302—3307).— ψ -Phenols do not condense so readily with phenols as with tertiary aromatic amines (*Abstr.*, 1904, i, 995). The mixture has to be heated for several hours at 100 — 150° in the absence of a solvent. The products are diphenylmethane derivatives, and as a rule pure products can only be isolated when the phenol has only one ortho-hydrogen or the para-hydrogen atom unsubstituted. In certain cases, 2 mols. of ψ -phenol react yielding bis-derivatives, which are more sparingly soluble.

3:5-Dibromo-4-hydroxybenzyl bromide (*Abstr.*, 1903, i, 621) and *o*-cresol yield a product melting at 99 — 105° and consisting probably of a mixture of *o*- and *p*-dibromohydroxybenzylcresols.

With *p*-cresol, 3':5'-bis-3:5-dibromo-4-hydroxybenzyl-*p*-cresol,



is obtained; it crystallises from benzene in colourless needles melting at 201 — 203° , and readily soluble in alcohol, ether, or acetic acid. The *tribenzoate*, $\text{C}_{42}\text{H}_{28}\text{O}_6\text{Br}_4$, crystallises from acetic acid in glistening needles, melts at 201 — 202° , and is insoluble in alkalis. When reduced with sodium and boiling alcohol, the tetrabromo-derivative yields bis-*p*-hydroxybenzyl-*p*-cresol, $\text{C}_6\text{H}_2\text{Me}(\text{OH})\cdot(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$, melting at 212 — 214° . The *triacetate*, $\text{C}_{27}\text{H}_{26}\text{O}_6$, melts at 117 — 118° .

*Dibromohydroxybenzyl-*p*-cresol* (3:5-dibromo-4:2'-dihydroxy-5'-methyl-diphenylmethane), $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$, which is also obtained

from *p*-cresol, melts at 105—106.5° and is readily soluble in most organic solvents.

Bisdibromohydroxybenzyl-p-xenol, $C_{22}H_{18}O_3Br_4$, obtained from the ψ -phenol and *p*-xynol, melts at 205°, and the corresponding *mono*-derivative, $C_{15}H_{14}O_2Br_2$, at 153—155°.

Dibromohydroxybenzyl- ψ -cumenol, $C_{16}H_{16}O_2Br_2$, crystallises from a mixture of light petroleum and benzene in pale rose-coloured plates melting at 146°.

β -Naphthol yields the *mono*-derivative, $OH \cdot C_6H_2Br_2 \cdot CH_2 \cdot C_{10}H_6 \cdot OH$, melting at 168—169°. The *diacetate* melts at 159—160°. J. J. S.

Action of Methyl Alcohol on Hexabromo-*o*-quinocatechol Ether. C. LORING JACKSON and PHILIP A. SHAFFER (*Amer. Chem. J.*, 1905, 34, 460—467).—An improved method is described for the preparation of hexabromo-*o*-quinocatechol ether, first prepared by Jackson and Koch (*Abstr.*, 1901, i, 597). When this compound is left in contact with methyl alcohol, a reaction takes place very slowly with formation of the additive *compound*, $C_{12}O_4Br_6 \cdot 2MeOH$, which crystallises from alcohol in white, rhombic plates, melts and decomposes at 220—221°, and is soluble in benzene or acetone, soluble to the extent of 4.3 per cent. in boiling alcohol, and insoluble in water. This compound is best obtained by adding solution of sodium methoxide to the hexabromo-*o*-quinocatechol ether suspended in methyl alcohol and treating the product with hydrochloric or sulphuric acid; the *sodium* derivative, $C_{12}O_4Br_6 \cdot MeOH \cdot MeONa$, is unstable, and on decomposition yields a *substance* which crystallises in red needles, decomposes at about 280°, and is soluble in water or alcohol. By the action of methyl alcohol and bromine on the methyl alcohol additive compound, a *substance* is formed which melts at about 150°. When phenylhydrazine is added slowly to a mixture of hexabromo-*o*-quinocatechol ether and nitrobenzene, hexabromodihydroxycatechol ether is produced; this reaction furnishes a convenient method for the preparation of this substance. E. G.

Action of Dilute Nitric Acid on Guaiacolsulphonic Acid. OTTO KÜHLING (*Ber.*, 1905, 38, 3007—3008. Compare Armstrong, this Journal, 1871, 24, 112).—When boiled with dilute nitric acid, potassium guaiacolsulphonate yields dinitroguaiacol, melting at 123—124° (Herzig, *Abstr.*, 1883, 464), and *dinitrodihydroxydimethoxydiphenyl*, $OH \cdot C_6H_2(NO_2)(OMe) \cdot C_6H_2(NO_2)(OMe) \cdot OH$, which forms a yellow, crystalline powder, melts and decomposes at 283°, and dissolves in aqueous alkali hydroxides to form red solutions. G. Y.

Condensation of Pyrogallol with Acetone and with Methyl Ethyl Ketone. RUDOLF FABINYI and TIBOR SZEKI (*Ber.*, 1905, 38,

3527—3531).—The compound $C_6(OH)_3 \begin{matrix} \diagup CMe_2 \\ | CMe_2 \\ \diagdown CMe_2 \end{matrix} C_6(OH)_3$, prepared

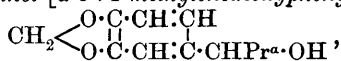
by heating a mixture of pyrogallol, acetone, and acetic and hydrochloric acids in a sealed tube at 145° during three-quarters of an hour, crystallises from acetic acid in slender, brownish- or reddish-white crystals,

and melts and decomposes at 260—265°. The *hexa-acetyl* derivative, $C_{33}H_{36}O_{12}$, separates from methyl alcohol in colourless scales and melts without decomposition at 247—248°. The *hexabenzoyl* derivative, $C_{63}H_{48}O_{12}$, separates from a mixture of acetic acid, nitrobenzene, and alcohol in minute, colourless scales and melts at 289°. The *dibromo*-derivative, $C_{21}H_{22}O_6Br_2$, forms small, bluish-white needles and melts and decomposes at 197—200°. Its *hexa-acetyl* derivative, $C_{33}H_{34}O_{12}Br_2$, separates from alcohol or acetic acid in white, glistening scales and melts at 260°.

The *condensation product*, $C_{24}H_{30}O_6$, from pyrogallol and methyl ethyl ketone, crystallises from acetic acid and melts and decomposes at 260°. Its *hexa-acetyl* derivative crystallises from dilute acetic acid in slender, white needles and melts at 212°. T. M. L.

Decomposition of *m*- and *p*-Nitrobenzyl Alcohols under the Influence of Aqueous and of Alcoholic Sodium Hydroxide. PAUL CARRÉ (*Compt. rend.*, 1905, 141, 594—596. Compare this vol., i, 307).—*m*- and *p*-Nitrobenzyl alcohols are decomposed less readily than the *o*-compound by the action of alkali hydroxides, and the products are less complex; *m*-nitrobenzyl alcohol, when heated at 100° with aqueous 10 per cent. sodium hydroxide, yields *m*-nitrobenzoic acid, *m*-azoxybenzoic acid, and *m*-azoxybenzyl alcohol, $ON_2(C_6H_4 \cdot CH_2 \cdot OH)_2$, which crystallises from benzene in long, yellow needles melting at 86° and forms a *dibenzoyl* derivative melting at 97°; under the action of alcoholic sodium hydroxide, *m*-nitrobenzyl alcohol yields *m*-azobenzoic acid and *m*-azobenzyl alcohol, $N_2(C_6H_4 \cdot CH_2 \cdot OH)_2$, which crystallises from benzene in beautiful orange needles melting at 106° and forms a *dibenzoyl* derivative crystallising in orange plates and melting at 124°. *p*-Nitrobenzyl alcohol is decomposed by aqueous sodium hydroxide with the formation of *p*-nitrobenzoic acid, *p*-azobenzoic acid, *p*-azobenzyl alcohol, *p*-azobenzaldehyde, and a compound melting at 224°, which is probably identical with *p*-nitrobenzaldoxime-*N*-*p*-formylphenyl-ether, described by Alway (compare Abstr., 1903, i, 706). When acted on by alcoholic sodium hydroxide, the products are *p*-azobenzoic acid and *p*-azobenzyl alcohol, which forms a *dibenzoyl* derivative crystallising from alcohol in red needles melting at 164°. M. A. W.

Action of Magnesium Propyl Iodide on Piperonaldehyde. EFISIO MAMELI and EZIO ALAGNA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 170—180. Compare Abstr., 1904, i, 1023; this vol., i, 203).—*Piperonylpropylcarbinol* [α -3 : 4-methylenedioxyphenylbutane- α -ol],



prepared by the action of piperonal (0.5 mol.) on magnesium propyl iodide (1 mol.) in ethereal solution with subsequent decomposition by means of ice and dilute sulphuric acid, is a straw-yellow oil boiling at 170—173° under 20 mm. pressure; it is readily oxidised to the corresponding ketone and, when distilled under diminished pressure or treated in the cold with gaseous hydrogen chloride and the product subsequently distilled, it gives α -piperonylbutylene (*vide infra*). The *acetate*, $CH_2O_2 \cdot C_6H_3 \cdot CHPr^{\alpha} \cdot OAc$, is a colourless oil boiling at

197—198° under 25 mm. pressure and dissolves in alcohol, but does not decolorise bromine. When treated with alcoholic potassium hydroxide solution, it yields acetic acid, water, and α -piperonyl- Δ^a -butylene, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{CHEt}$, which is a colourless oil with a pleasant odour, is soluble in alcohol, ether, or benzene in all proportions, and boils at 164—166° under 25 mm. or at 258—259° under the ordinary pressure; it is volatile in a current of steam, has the sp. gr. 1.0964 at 15°, and exhibits normal cryoscopic behaviour in benzene solution; it rapidly reduces potassium permanganate and absorbs bromine and hydrogen bromide. With picric acid it combines, giving the *picrate*, $\text{C}_{11}\text{H}_{13}\text{O}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, which crystallises in large, cherry-red prisms melting at 67°.

α -Piperonylbutane, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Pr}^a$, prepared by reducing piperonylbutylene by means of sodium in alcoholic solution, is a colourless oil boiling at 246—250°.

$\alpha\beta$ -Dibromo- α -piperonylbutane, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CHBr} \cdot \text{CHBrEt}$, obtained by the action of bromine on piperonylbutylene, is a dark oil which decomposes on distillation.

Piperonyl propyl ketone, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{COPr}^a$, prepared by the oxidation of piperonylpropylcarbinol with chromic acid, separates from alcohol or light petroleum in crystals melting at 47° and is readily soluble in ether or benzene, and to a less extent in acetic acid. Its *oxime*, $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$, is deposited from alcohol in crystals melting at 75° and is slightly soluble in water and more readily in ether or benzene. The *semicarbazone*, $\text{C}_{12}\text{H}_{13}\text{O}_3\text{N}_3$, crystallises from aqueous alcohol in tufts of small needles melting at 193—194°. T. H. P.

Some Derivatives of cycloHexane. PAUL FREUNDLER and E. DAMOND (*Compt. rend.*, 1905, 141, 593—594).—Bromocyclohexane, $\text{C}_6\text{H}_{11}\text{Br}$, prepared by the action of phosphorus tribromide on cyclohexanol, boils at 61—62° under 20 mm. pressure, and the yield is 68 per cent.; iodicyclohexane, $\text{C}_6\text{H}_{11}\text{I}$, similarly obtained by the prolonged action of phosphorus diiodide on cyclohexanol, boils at 84—86° under 23—24 mm. pressure, and the yield is 87 per cent. (compare Baeyer, *Abstr.*, 1894, i, 175). Ethyl α -cyanocyclohexylacetate, $\text{C}_6\text{H}_{11} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$, obtained by heating the sodium derivative of ethyl cyanoacetate with chloro- or iodo-cyclohexane in xylene solution at 145—150°, is a colourless liquid boiling at 158—161° under 23—24 mm. pressure; ethyl cyclohexylmalonate, $\text{C}_6\text{H}_{11} \cdot \text{CH}(\text{CO}_2\text{Et})_2$, similarly prepared from the sodium derivative of ethyl malonate, boils at 148—151° under 16—17 mm. pressure. cycloHexylacetic acid [hexahydrophenylacetic acid], $\text{C}_6\text{H}_{11} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by heating cyclohexylmalonic acid at 190° or by boiling ethyl cyclocyanoacetate with dilute sulphuric acid, crystallises in white plates melting at 27°, boils at 244—246°, and is readily soluble in the ordinary organic solvents; ethyl cyclohexylacetate is a liquid with an agreeable odour boiling at 211—212° under 766 mm. pressure. M. A. W.

Hofmann's Reaction. ERNST MOHR (*J. pr. Chem.*, 1905, [ii], 72, 297—306. Compare this vol., i, 274; Graebe and Rostovzeff, *Abstr.*, 1902, i, 663; Hantzsch, *Abstr.*, 1903, i, 29).—When one mol. of

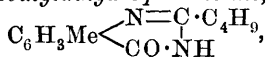
benzoylchloroamide is dissolved in one mol. of sodium hydroxide in 2*N* aqueous solution, heat is developed, together with an intense odour of phenylcarbimide; moreover, when a freshly-prepared solution of benzoylchloroamide in aqueous sodium hydroxide is distilled in a current of steam, the distillate contains an oil which solidifies partly in the condenser, forming *s*-diphenylcarbamide; this is found, together with benzoylphenylcarbamide, also in the distillation residue (compare Hofmann, Abstr., 1882, 822; Dam and Aberson, Abstr., 1901, ii, 88). Phenylcarbimide is formed, therefore, as an intermediate product of the action of alkali hydroxides on benzoylchloroamide. Its formation similarly in the action of alkali hydroxides on dibenzhydroxamic acid is proved also by distillation with steam, when diphenylcarbamide is obtained from the distillate. G. Y.

Some Acyl Derivatives of Homoanthranilonitrile [3-Amino-*p*-toluonitrile] and the 4-Keto-7-methyldihydroquinazolines prepared therefrom. MARSTON T. BOGERT and ALFRED HOFFMAN (*J. Amer. Chem. Soc.*, 1905, 27, 1293—1301. Compare Niementowski, Abstr., 1888, 837; 1889, 1065; 1895, i, 571).—3-Nitro-*p*-toluonitrile crystallises from water in needles of a faint green tint and melts at 99·8° (all the melting points given are corrected). Homoanthranilonitrile (3-amino-*p*-toluonitrile) crystallises from carbon disulphide in large, yellow crystals and melts at 94°.

The following acyl derivatives of homoanthranilonitrile have been prepared by heating the nitrile with acid anhydrides. The *acetyl* derivative, $\text{CN} \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NHAc}$, melting at 136°, the *propionyl* derivative (m. p. 138°), the *isobutyryl* derivative (m. p. 144°), and the *isovaleryl* derivative (m. p. 139°). The following derivatives have been prepared by the action of acyl chlorides on homoanthranilonitrile. The *benzoyl* derivative (m. p. 145°), the *m*-nitrobenzoyl derivative (m. p. 218°), and the *p*-nitrobenzoyl derivative (m. p. 223°). The formyl derivative cannot be obtained by the action of glacial formic acid on homoanthranilonitrile, but 4-keto-7-methyldihydroquinazoline is produced.

When the acyl derivatives of homoanthranilonitrile are heated with a solution of potassium hydroxide and hydrogen peroxide, quinazolines are produced. Acetylhomoanthranilonitrile yields 4-keto-2:7-dimethyldihydroquinazoline, whilst the propionyl and isobutyryl derivatives furnish 4-keto-2-ethyl- and 2-isopropyl-7-methyl-dihydroquinazoline respectively. All these compounds have been described by Niementowski.

4-Keto-7-methyl-2-isobutyldihydroquinazoline,



crystallises in needles, melts at 219°, and dissolves readily in acetone, acetic acid, or alcohol. 4-Keto-2-phenyl-7-methyldihydroquinazoline crystallises in plates or needles, melts at 243°, and is easily soluble in chloroform, hot benzene, alcohol, or acetic acid. The corresponding 2-*m*-nitrophenyl and 2-*p*-nitrophenyl derivatives form microcrystalline powders, melt sharply above 370°, and are easily soluble in acetone, chloroform, acetic acid, or alcohol. E. G.

Separation of Cinnamic Acid into Stereoisomeric Components. EMIL ERLÉNMEYER, jun. (*Ber.*, 1905, 38, 3499—3503).—The brucine salt of cinnamic acid proved to be homogeneous when prepared in solution in benzene, and melted at $92-93^{\circ}$; by working in alcoholic solution, isomeric crystalline salts were obtained, which differed in melting point and rotatory power; thus samples were obtained having $[\alpha]_D$ 0° , -10.84° , $+8.82^{\circ}$, -8.67° , and the melting points 135° , 113° , 135° , 107° . All these salts gave an inactive cinnamic acid, but the author is of opinion that the latter is a mixture of enantiomorphous isomerides the optical activity of which is too small to be measured.

T. M. L.

Second Stereoisomeric Component of *allo*Cinnamic Acid. EMIL ERLÉNMEYER, jun. (*Ber.*, 1905, 38, 3496—3499).—The crystalline brucine salt derived from *allocinnamic* acid (this vol., i, 646) yields an acid which differs in a marked way from the *isocinnamic* acid isolated by Liebermann from the coca plant. The acid contained in the more soluble brucine salt has now been investigated, and proved by crystallographic measurements to be identical with Liebermann's acid. Although neither acid shows a measurable optical activity, they are regarded by the author as optical isomerides; this conclusion is based in part on the observation that the brucine salts differ considerably in rotatory power, namely, $[\alpha]_D$ -24.89° and -13.98° .

T. M. L.

Action of Hippuryl Chloride on Polyhydric Phenols. EMIL FISCHER (*Ber.*, 1905, 38, 2926—2934. Compare this vol., i, 263).—*o*-Hydroxyphenyl hippurate, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is formed when hippuryl chloride is heated with catechol on the water-bath; it crystallises from water in delicate, colourless leaflets, melts at $134-136^{\circ}$ (corr.), is readily soluble in alcohol or dilute alkali hydroxides, and is easily hydrolysed by warm dilute acids or alkali hydroxides or by cold concentrated sulphuric acid. When treated with hydrogen chloride in a tube cooled by liquid air, then sealed and kept at $20-30^{\circ}$ for 16 days, it forms the *anhydro*-derivative, $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$, which crystallises from ethyl acetate in colourless, slender needles, sinters at 226° (corr.), and melts at $232-233^{\circ}$ (corr.); it gives with alcoholic ferric chloride a dark coloration, and on addition of water a deep brownish-red precipitate, decolorises alkaline potassium permanganate at the ordinary temperature, and remains almost unchanged when heated with hydrogen chloride in glacial acetic acid solution in a sealed tube at 100° .

When heated with hippuryl chloride on the water-bath, resorcinol forms one dihippuryl and two monhippuryl derivatives. The α -hippuryl derivative, $\text{C}_{15}\text{H}_{13}\text{O}_4\text{N}$, which is extracted from the reaction-product by means of cold ethyl acetate, crystallises on concentration of the solution, melts at 144° (corr.), is decomposed by aqueous alkali hydroxides, and is hydrolysed with formation of hippuric acid when boiled with dilute hydrochloric acid. The β -hippuryl derivative crystallises from alcohol in colourless, slender needles, commences to decompose at 255° (corr.), and when quickly heated melts at about

274° (corr.); it dissolves in dilute sodium hydroxide and is precipitated unchanged on acidification, gives a brownish-red coloration with alcoholic ferric chloride, and is much more stable than the α -isomeride towards boiling hydrochloric acid. The *dihippuryl* derivative, $C_{24}H_{20}O_6N_2$, remains after successive treatment of the reaction product with cold ethyl acetate and dilute sodium hydroxide; it crystallises from hot ethyl acetate in glistening leaflets, melts at 179—180° (corr.), is readily soluble in alcohol, but only sparingly so in hot water or ether, is decomposed by boiling dilute alkali hydroxides, and dissolves in cold concentrated sulphuric acid, from which it is precipitated unchanged on dilution. Hippuryl chloride reacts with quinol at 125—130° to form hippuryl and dihippuryl derivatives of quinol. The *hippuryl* derivative, $C_{15}H_{13}O_4N$, crystallises from water in glistening needles, melts at 155—157° (corr.), is readily soluble in cold alcohol, ethyl acetate, hot glacial acetic acid, or dilute alkali hydroxides, and is easily hydrolysed by boiling hydrochloric acid with formation of hippuric acid. The *dihippuryl* derivative, $C_{24}H_{20}O_6N_2$, crystallises from boiling alcohol in glistening, white leaflets, commences to sinter at 214° (corr.), and melts and decomposes at 220—222° (corr.); it is only sparingly soluble in hot water, boiling alcohol, ether, acetone, or hot toluene, and is hydrolysed with formation of hippuric acid by boiling aqueous alkali hydroxides. G. Y.

Action of Potassium Hypochlorite, Hypobromite, and Hypoiodite on Dipotassium Salicylate. LASSAR-COHN and FRITZ SCHULTZE (*Ber.*, 1905, 38, 3294—3302).—When ice-cold aqueous solutions of potassium hypobromite and dipotassium salicylate are mixed in molecular proportions and the mixture acidified, the products are 6-bromo- and 5:6-dibromosalicylic acid. These may be separated by means of their ammonium salts, as *ammonium 5:6-dibromosalicylate* is very sparingly soluble in water, 0.44 gram dissolving in 100 c.c. of water at 16°. The monobromo-acid melts at 161° and begins to sublime at 100°; the dibromo-acid melts at 227.5°, and when heated for 24 hours at 280° with concentrated hydrochloric acid yields 3:4-dibromophenol. The *methyl* ester melts at 156°. Neither acid can be esterified by the hydrogen chloride catalytic method.

When an excess (2—4 mols.) of the hypobromite is used, a certain amount of *s*-tribromophenol is formed, but no monobromo-acid.

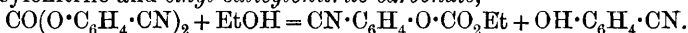
Potassium hypochlorite yields a mixture of 6-chloro- and 5:6-dichloro-salicylic acids, which can also be separated by means of their ammonium salts. The dichloro-acid melts at 223°, is sparingly soluble in water, cannot be esterified by Fischer and Speier's method, and is not decomposed when heated with hydrochloric acid at 300°. When fused with potassium hydroxide and nitrated, it yields a *dichloronitrophenol* melting at 125°. The *barium* salt is anhydrous and crystallises from water, and the *methyl* ester melts at 150°. The monochloro-acid melts at 176° and when heated with hydrochloric acid yields *m*-chlorophenol. When 4 mols. of the hypochlorite are used, considerable quantities of *s*-trichlorophenol are produced.

The product obtained by mixing molecular proportions of potassium hypoiodite and dipotassium salicylate, then adding potassium hydrogen

sulphite and fractionally precipitating with acid, is 4-iodosalicylic acid. This melts at 199.5° and when heated with hydrochloric acid at 300° yields *m*-iodophenol. The aniline salt, $\text{OH}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CO}_2\cdot\text{NH}_3\text{Ph}$, melts at 138° and the methyl ester at 80° . J. J. S.

Benzoyl Derivatives of Salicylamide. KARL AUWERS (*Ber.*, 1905, 38, 3256—3259).—A discussion of Titherley and Hicks' paper (*Trans.*, 1905, 87, 1207). The author considers that the labile benzoyl derivative of salicylamide has the constitution $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, whilst the stable isomeride, melting at 208° , is the *N*-benzoyl derivative, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHBz}$. G. Y.

Carbonates of Salicylonitrile and of Salicylaldehyde. ALFRED EINHORN and GUSTAV HAAS (*Ber.*, 1905, 38, 3627—3632. Compare *Abstr.*, 1903, i, 30).—*Salicylonitrile carbonate*, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CN})_2$, is obtained by shaking a toluene solution of carbonyl chloride with a solution of salicylonitrile in sodium hydroxide and adding light petroleum to the toluene solution. It crystallises from alcohol in colourless, felted needles, melts at 116° , and dissolves readily in benzene, chloroform, or ether. When warmed with water or left in contact with alkalis, it is slowly decomposed, yielding salicylonitrile. It is readily decomposed when warmed with absolute alcohol, yielding salicylonitrile and *ethyl salicylonitrile carbonate*,



The latter crystallises in needles, melts at 47° , is insoluble in water, but dissolves readily in alcohol or ether.

Hydrogen peroxide reacts with a cold alcoholic solution of the carbonate, yielding salicylonitrile. Concentrated sulphuric acid converts the carbonate of the nitrile into salicylamide carbonate.

When salicylaldehyde is warmed with a pyridine solution of carbonyl chloride, disalicylaldehyde is formed; with a solution of sodium hydroxide instead of pyridine, *salicylaldehyde carbonate*, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO})_2$, is obtained. It crystallises from light petroleum in colourless, felted needles, or from carbon tetrachloride in large rhombohedra melting at 88 — 89° . It dissolves readily in acetone, benzene, chloroform, or ethyl acetate, but only sparingly in alcohol. It cannot be oxidised to the corresponding carbonate of salicylic acid.

The *dioxime*, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{OH})_2$, crystallises from methyl alcohol in colourless needles melting at 121 — 122° . It dissolves readily in most organic solvents and is decomposed by sodium hydroxide. The *bisphenylhydrazone*, $\text{C}_{27}\text{H}_{22}\text{O}_3\text{N}_2$, crystallises in yellow plates and melts at 179 — 180° . The dihydrazone and disemicarbazone could not be prepared.

The conversion of Titherley and Hicks' *O*-benzoylsalicylamide melting at 144° into the isomeride melting at 208° (*Trans.*, 1905, 87, 1207) is regarded as the conversion of an *O*- into an *N*-benzoyl derivative. (Compare Auwers, preceding abstract.) J. J. S.

Constitution of the Aromatic Purpuric Acids. VII. Ethyl 3:5-dinitrosalicylate and Potassium Cyanide. WALTHER BORSCHKE and G. GAHRTZ (*Ber.*, 1905, 38, 3538—3542. Compare *Abstr.*, 1904, i, 166, 574; this vol., i, 51).—Ethyl 5-nitro-4-cyano-3-

hydroxylamino-2-hydroxybenzoate, formed by reducing dinitrosalicylic ester with potassium cyanide, can be purified by crystallising from ethyl alcohol; it then forms reddish-brown scales and melts at 186° . Saponification not only separates alcohol, but results in the addition of a molecule of water to the cyano-group,
 $\text{NO}_2 \cdot \text{C}_6\text{H}(\text{CN})(\text{NH} \cdot \text{OH})(\text{OH}) \cdot \text{CO}_2\text{Et} \rightarrow$

$\text{NO}_2 \cdot \text{C}_6\text{H}(\text{CO} \cdot \text{NH}_2)(\text{NH} \cdot \text{OH})(\text{OK}) \cdot \text{CO}_2\text{K}$;
 the *potassium* salt separates with $1\text{H}_2\text{O}$; the free nitrocarbamido-hydroxylaminohydroxybenzoic acid separates from alcohol in blood-red needles and melts at $187\text{--}188^{\circ}$.

The original ester is oxidised by nitric acid to *ethyl 3:5-dinitro-4-cyano-salicylate*, $\text{OH} \cdot \text{C}_6\text{H}(\text{NO}_2)_2(\text{CN}) \cdot \text{CO}_2\text{Et}$, which crystallises from alcohol or acetic acid in stout, dark red needles and melts at 187° . The *ammonium* salt was prepared and analysed. The *aniline* salt of the ester crystallises in slender, red needles and melts at 162° .

Sulphuric acid causes the original ester to undergo isomeric change (compare β -phenylhydroxylamine \rightarrow *p*-aminophenol). The product, *ethyl 5-nitro-3-amino-4-cyano-2:6-dihydroxybenzoate*,

$\text{NO}_2 \cdot \text{C}_6(\text{OH})_2(\text{CN})(\text{NH}_2) \cdot \text{CO}_2\text{Et}$,
 crystallises from alcohol in brownish-red needles and melts at $199\text{--}200^{\circ}$; the *ammonium* salt, $\text{C}_{10}\text{H}_8\text{O}_6\text{N}_3 \cdot \text{NH}_4$, forms slender, red needles. The isomeric change here recorded affords the first proof of the presence of a hydroxylamino-group in the aromatic purpuric acids.

T. M. L.

***o*-Benzoylbenzoic Acid.** HUGO LANG (*Monatsh.*, 1905, 26, 971—976. Compare Basler Chemische Fabrik, Abstr., 1904, i, 512; Kliegl, this vol., i, 187).—4-Nitro-2-benzoylbenzoic acid is formed when anhydrous *o*-benzoylbenzoic acid is added to nitric acid of sp. gr. 1.52, cooled by ice, and after four to five hours the reaction product poured into ice-water; after recrystallisation from benzene, it melts at $160\text{--}161^{\circ}$ (m. p. $161.5\text{--}162^{\circ}$; Kliegl, *loc. cit.*), but on recrystallisation from alcohol forms yellow prisms and melts at $183\text{--}184^{\circ}$. The methyl ester, formed by boiling the acid with methyl alcohol and a few c.c. of concentrated sulphuric acid, melts at 105° . The isomeric *methyl* ester, obtained by Meyer's thionyl chloride method (Abstr., 1904, i, 747), crystallises in large, monoclinic prisms and melts at 131° . 4-Nitro-2-benzoylbenzoyl chloride, formed by the action of thionyl chloride on the acid, decomposes at $127\text{--}129^{\circ}$, or on exposure to the air.

The action of nitric acid of sp. gr. 1.52 on methyl *o*-benzoylbenzoate leads to the formation of a *dinitro*-derivative, $\text{C}_{15}\text{H}_{10}\text{O}_7\text{N}_2$, which crystallises in glistening, white leaflets, melts and decomposes at 136° , and is readily soluble in alcohol, chloroform, or hot benzene.

G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids.
XIII. Ester-acids of 4-Substituted Phthalic Acids. RUDOLF WEGSCHEIDER and ERICH BONDI (*Monatsh.*, 1905, 26, 1039—1068. Compare Wegscheider and Lipschitz, Abstr., 1901, i, 32; Wegscheider, Abstr., 1902, i, 618; Wegscheider and Piesen, *ibid.*, i, 619; Weg-

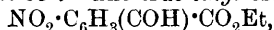
scheider and Kušý von Dúbrav, Abstr., 1904, i, 244).—Contrary to the statements of Miller (Abstr., 1878, 982) and of Bogert and Boroschek (Abstr., 1902, i, 98), the action of ethyl alcohol and hydrogen chloride on 4-nitrophthalic acid and of ethyl alcohol on the anhydride of 4-nitrophthalic acid leads to the formation of the 1-monoethyl ester melting at 127—128°. Only by the latter method of esterification could be isolated a small quantity of the 2-monoethyl ester melting at 137°. Bogert and Boroschek's substance melting at 141—150° was a mixture.

1-Ethyl hydrogen 4-nitrophthalate [$\text{CO}_2\text{Et} : \text{CO}_2\text{H} : \text{NO}_2 = 1 : 2 : 4$] crystallises in monoclinic plates [$a : b : c = 1.7447 : 1 : 1.4277$; $\beta = 118^\circ 31'$].

The ψ -ethyl ester of 5-nitrophthalaldehydic acid,



is formed by boiling the acid with alcohol in a reflux apparatus; it crystallises from a mixture of benzene and light petroleum in sheaves of needles and melts at 95°. The true *ethyl* ester,



is formed, along with a yellow, amorphous substance which softens at 145° and melts at 160°, and decomposes with evolution of a gas at 165—170°, by the action of ethyl iodide on the silver salt. It crystallises from a mixture of benzene and light petroleum in slender, colourless needles, melts at 71—72°, and is oxidised by potassium permanganate to 2-ethyl hydrogen 4-nitrophthalate [$\text{CO}_2\text{H} : \text{CO}_2\text{Et} : \text{NO}_2 = 1 : 2 : 4$], which melts at 137°.

When reduced with stannous chloride and hydrochloric acid or with zinc dust and methyl-alcoholic hydrochloric acid, 1-methyl hydrogen 4-nitrophthalate yields 1-methyl hydrogen 4-aminophthalate, $\text{C}_9\text{H}_9\text{O}_4\text{N}$, which is obtained on evaporation of its blue, fluorescent ethereal solution as a yellow, crystalline substance; different fractions melted at from 110° to 145°. When diazotised in dilute sulphuric ester and warmed finally at 100°, the amino-ester yields 1-methyl hydrogen 4-hydroxyphthalic acid, $\text{C}_9\text{H}_8\text{O}_5$, which is obtained as a slightly yellow, crystalline substance decomposing at 159—160°; this is isomeric with Wegscheider and Piesen's α -ester melting at 166° (*loc. cit.*). G. Y.

Nitro-derivatives of Fluorescein. MARSTON T. BOGERT and RALPH GARRIGUE WRIGHT (*J. Amer. Chem. Soc.*, 1905, 27, 1310—1316).—This work was undertaken with the object of ascertaining the influence of nitro- and amino-groups on the fluorescence of fluorescein.

3- and 4-Nitrofluoresceins, obtained by the interaction of resorcinol with 3-nitrophthalic acid and 4-nitrophthalic acid respectively, dissolve in alkalis to form yellowish-red solutions with a weak but distinct green fluorescence.

Dinitrofluorescein (Hewitt and Perkin, *Trans.*, 1900, 77, 1324) dissolves in alkali with formation of a deep blue solution which shows no fluorescence.

An attempt was made to prepare tetranitrofluorescein (Baeyer, this *Journal*, 1877, i, 200, and Hewitt and Perkin, *loc. cit.*) by the action of fuming nitric acid on a solution of fluorescein in sulphuric acid. The

product crystallised from acetone as a white powder with a distinct yellowish-green fluorescence, and on analysis gave results agreeing with those required for a pentanitro- rather than a tetranitro-compound. The acetyl derivative of this compound furnished analytical data corresponding with those required for a pentanitrotetra-acetyl-fluorescein.

When 4-nitrofluorescein is reduced with stannous chloride and hydrochloric acid, a *substance*, probably the aminofluorescein, is formed which melts at 281° and dissolves in alkalis with a green fluorescence. On reducing 3-nitrofluorescein, a product was obtained which gave a fluorescent solution in alkali, but the amino-derivative itself could not be isolated.

By the reduction of dinitrofluorescein with stannous chloride and hydrochloric acid, a *substance* is obtained which crystallises from alcohol in blue plates with brilliant, bronze-green lustre, melts at $198-199^{\circ}$, is slightly soluble in ether or glacial acetic acid, forming solutions with a strong, green fluorescence, and in dilute alkalis with production of red solutions with violet fluorescence. When an alcoholic solution of dinitrofluorescein is reduced with stannous chloride and dry hydrogen chloride, a *substance* is produced which forms bright yellow crystals and melts at 249° .

By the action of various reducing agents on pentanitrofluorescein, deep red solutions were obtained which, on dilution, showed a blue fluorescence, but no pure reduction product could be isolated.

E. G.

Products obtained by the Autoxidation of Eosin. ARTHUR HEFFTER (*Ber.*, 1905, **38**, 3633—3634. Compare Gros, *Abstr.*, 1901, ii, 433).—When a 0.5 per cent. eosin solution containing 1 per cent. of sodium hydroxide is exposed to sunlight, and air is passed through the solution until the fluorescence has completely disappeared and the red colour has been bleached to a pale yellow, no precipitate is obtained and the solution is found to contain sodium bromide, carbonate, oxalate, and phthalate. From 30 grams of eosin, 1.1 grams of phthalic acid were obtained.

J. J. S.

Formation of $\alpha\beta$ -Dihydrocinnamylidenemalononic Acid and $\alpha\beta$ -Dihydrocinnamylideneacetic Acid. EMIL ERLÉNMEYER, jun. and ADOLF KREUTZ (*Ber.*, 1905, **38**, 3503—3505).— $\alpha\beta$ -Dihydrocinnamylidenemalononic acid, prepared by condensing styryl chloride with ethyl malonate and saponifying the ester, separates from benzene in slender needles and decomposes at 132° , thus differing essentially from the $\alpha\delta$ - and $\gamma\delta$ -acids. On heating to drive off carbon dioxide, an acid is obtained identical with the $\alpha\beta$ -dihydrocinnamylideneacetic acid described by Fichter and Baur (*Abstr.*, 1898, i, 662) and by Riiber (this vol., i, 777).

T. M. L.

Two Dehydropinacones of Artemisin (Artemisone and iso-Artemisone). PASQUALE BERTOLO and G. RANFALDI (*Gazzetta*, 1905, **35**, ii, 235—244. Compare Bertolo, *Abstr.*, 1902, i, 814).—The reduction of artemisin by means of zinc dust and acetic acid yields a bis-hypo-artemisin, which the authors term *artemisone*, of the com-

position $C_{30}H_{34}O_6$. It separates from alcohol in minute, white crystals, to some extent grouped in small, mammillary masses, and melts at $273-274^\circ$. It dissolves slightly in ether, light petroleum, or chloroform, and more readily in acetic acid, in which it has $[\alpha]_D +159^\circ$. Artemisone preserves the lactonic character of artemisin and dissolves in alkaline hydroxide solutions forming salts of a dibasic acid, *artemisonic acid*, which, unlike the corresponding acid obtained from santonone, is only slightly stable in the free state, as it gradually loses water and becomes converted into *isoartemisonone* (*vide infra*). The barium, $C_{30}H_{36}O_8Ba$, and silver salts, $C_{30}H_{36}O_8Ag_2$, of artemisonic acid were prepared and analysed. With salts of the heavy metals, artemisonic acid gives variously coloured precipitates.

*iso*Artemisone is a lactone isomeric with artemisone and is best prepared by decomposing barium artemisonate by means of hydrochloric acid. It separates from a mixture of light petroleum and ether in minute, white crystals melting at $182-183^\circ$. It has the normal molecular weight in freezing acetic acid and has $[\alpha]_D -157^\circ$ in alcohol and -153° in glacial acetic acid. It is soluble in solutions of the alkali hydroxides or carbonates and is precipitated unchanged on addition of an acid. Like artemisone, it does not react with hydroxylamine, phenylhydrazine, or acetic anhydride.

On the supposition that artemisone and *iso*artemisonone were enantiomorphous compounds, attempts were made to prepare the corresponding racemic compound, but these were unsuccessful.

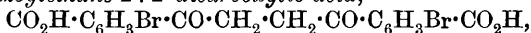
T. H. P.

Dibenzoylthane-2:2'-dicarboxylic Acid and its Anhydride.

ARNOLD REISSERT and W. ENGEL (*Ber.*, 1905, 38, 3281-3294).

—*Dibromoethinediphthalide*, $CO \langle \overset{C_6H_3Br}{\underset{O}{\text{C}}} \rangle C:C_2H_2:C \langle \overset{C_6H_3Br}{\underset{O}{\text{C}}} \rangle CO$,

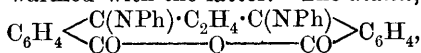
is formed by heating dibenzoylthane-2:2'-dicarboxylic acid with bromine in a sealed tube at 100° for 24 hours; it does not melt at 350° , and does not lose bromine when boiled with concentrated aqueous potassium hydroxide, aniline, or alcoholic ammonia. When boiled with 20 per cent. aqueous potassium hydroxide, it yields *dibromobenzoylthane-2:2'-dicarboxylic acid*,



which melts above 350° .

When dissolved in nitric acid of sp. gr. 1.5, dibenzoylthane-2:2'-dicarboxylic acid yields a *substance* which crystallises in large, monoclinic plates, decomposes and evolves nitric oxide at about 90° , after resolidification melts at $196-200^\circ$, and when treated with sodium carbonate forms Roser's β -anhydride melting at 202° (*Abstr.*, 1886, 243). This is formed also, sometimes together with a mixture melting at $220-230^\circ$, when the acid is boiled with acetic anhydride, or together with ethinediphthalide, when the acid is heated with hydrogen chloride in glacial acetic acid solution or with an excess of concentrated hydrochloric acid at 100° for four hours. When heated with concentrated hydrochloric acid at 100° for nine hours, the acid yields traces of a yellow *substance* melting at $225-230^\circ$, together with ethinediphthalide. The β -anhydride remains unchanged when

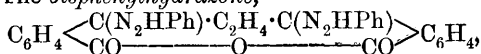
boiled for a short time with acetic anhydride, or glacial acetic and concentrated hydrochloric acids, or with glacial acetic and concentrated sulphuric acids. It melts without change, but when heated to the boiling point or dissolved in concentrated sulphuric acid it yields ethinephthalide, into which it is partly converted when boiled with an excess of concentrated hydrochloric acid for nine hours. Ethinephthalide is formed also when dibenzoylthane-2 : 2'-dicarboxylic acid is dissolved in a mixture of acetic anhydride and concentrated sulphuric acid or is warmed with the latter. The *dianil*,



is formed when the anhydride is heated with aniline on the water-bath; it crystallises from alcohol, decomposes at 190—191°, is easily soluble in glacial acetic acid, and only sparingly so in benzene, dissolves without formation of aniline in boiling sodium carbonate solution, and is hydrolysed by boiling sodium ethoxide solution.

Ethinediphtalidedianil, $\text{CO} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{N Ph} \end{array} \right\rangle \text{C} : \text{CH} : \text{CH} : \text{C} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{N Ph} \end{array} \right\rangle \text{CO}$, is

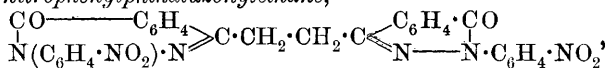
obtained when the anhydride is heated with aniline for three hours at 150—160°; it separates from glacial acetic acid in yellow crystals, melts at 310—311°, is stable towards alkali hydroxides and acids, and may be identical with Roser's diphthalylsuccindehydranilide (Abstr., 1886, 244). The *di-o-tolil*, $\text{C}_{32}\text{H}_{24}\text{O}_9\text{N}_2$, crystallises in stout, yellow needles and melts at 286—287°. The *di-p-tolil* melts at 294—295°. The *bisphenylhydrazone*,



formed when the anhydride is warmed with an excess of phenylhydrazine, is a colourless, crystalline substance, which melts at 242°, and dissolves in alcoholic potassium hydroxide, but after some time separates from the solution unchanged.

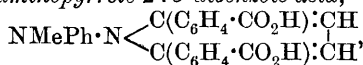
When warmed with nitric acid of sp. gr. 1·4, bisphenylphthalazonylethane, melting at 236—237°, yields a *dinitronitroso*-derivative, $\text{C}_{30}\text{H}_{10}\text{O}_7\text{N}_7$, which melts at 316—318°, and on reduction with stannous chloride forms a *base* which melts at 251—253°.

Bis-p-nitrophenylphthalazonylethane,



formed by boiling dibenzoylthanedio-carboxylic acid with *p*-nitrophenylhydrazine in alcoholic solution, melts above 350°.

1-Phenylmethylaminopyrrole-2 : 5-dibenzoic acid,



is obtained by boiling dibenzoylthane-2 : 2'-dicarboxylic acid with phenylmethylhydrazine in alcoholic solution in a reflux apparatus; it crystallises in slightly brown, stout needles and melts at 205—206°. If the acid is boiled with phenylmethylhydrazine in a limited quantity of

alcohol, it forms the *anhydride*, $\text{NMePh} \cdot \text{N} \left\langle \begin{array}{c} \text{C} \text{---} \text{C}_6\text{H}_4 \cdot \text{CO} \\ \text{C} \text{---} \text{C}_2\text{H}_2 \\ \text{C} \text{---} \text{C}_6\text{H}_4 \cdot \text{CO} \end{array} \right\rangle \text{O}$, which

crystallises in stout, yellow needles, melts at 205—206°, and is hydrolysed by aqueous alkali hydroxides. The *sodium* salt, $C_{25}H_{18}O_4N_2Na_2$, crystallises in thin, white leaflets; the *silver* salt, $C_{25}H_{18}O_4N_2Ag_2$, was analysed; the *diethyl* ester, crystallises in concentric aggregates of needles and melts at 90—91°. When treated with cooled concentrated sulphuric acid, the acid is decomposed with formation of methylaniline and *pyrrole-2:5-dibenzoic acid*, which is obtained as an amorphous substance melting and decomposing at 195° (compare Gabriel, *Ber.*, 1886, 19, 841).

1-*Phenylbenzylaminopyrrole-2:5-dibenzoic acid*, $C_{31}H_{24}O_4N_2$, formed by boiling dibenzoylthane-2:2'-dicarboxylic acid with phenylbenzylhydrazine in alcoholic solution, crystallises from dilute alcohol and melts at 218—219°. The *silver* salt, $C_{31}H_{22}O_4N_2Ag_2$, was analysed; the *diethyl* ester, $C_{35}H_{30}O_4N_2$, crystallises in slender, white needles and melts at 101—102°. When treated with concentrated sulphuric acid, the acid is decomposed with formation of pyrrole-2:5-dibenzoic acid, melting at 195°. G. Y.

Ellagic Acid. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1905, 26, 1139—1148. Compare Goldschmiedt and Jahoda, *Abstr.*, 1892, 990; Perkin and Nierenstein, *Trans.*, 1905, 87, 1412).—When boiled with phenylhydrazine in alcoholic solution, or when carefully heated with phenylhydrazine in absence of a solvent, ellagic acid forms the *product* $C_{14}H_6O_8, N_2H_3Ph$, which crystallises in microscopic, yellow needles, is decomposed partially when boiled with alcohol, and yields ellagic acid on addition of acetic acid to its suspension in water. Ellagic acid forms similar compounds with aniline and quinoline; the air-dried *product* with quinoline has the formula $2C_{14}H_6O_8, C_9H_7N$.

The etherification of ellagic acid by means of alkyl iodides and alcoholic alkali hydroxides takes place extremely slowly, and part of the acid undergoes decomposition; slightly better results are obtained by heating ellagic acid with alkyl iodides and aqueous potassium hydroxide at 150—160° under pressure. *Ellagic acid methyl ether*, $C_{14}H_5O_7 \cdot OMe$, formed in this manner, is obtained as a yellow, crystalline powder which decomposes without melting when heated gives no coloration with ferric chloride, and forms a *diacetate*, $C_{14}H_3O_7Ac_2 \cdot OMe$; this separates as a white, crystalline powder and melts when heated. *Ellagic acid dimethyl ether*, $C_{14}H_4O_6(OMe)_2$, formed in small quantity on prolonged heating of ellagic acid with methyl iodide and aqueous potassium hydroxide at 150—160°, is obtained as an insoluble, microcrystalline powder, which dissolves in concentrated sulphuric acid, from which it gradually separates in white crystals, and gives no coloration with ferric chloride.

The repeated action of diazomethane on ellagic acid in ethereal solution leads to the formation of *ellagic acid tetramethyl ether*, $C_{14}H_2O_4(OMe)_4$; this slowly separates from its solution in aqueous alkali hydroxides, on neutralisation with carbon dioxide or mineral acids and warming, in hair-like, almost colourless, microscopic needles which remain unchanged at 310°, is insoluble or almost so in aromatic hydrocarbons, alcohol, ether, chloroform, or carbon disulphide, dissolves in concentrated sulphuric acid to form a yellowish-green solution, from

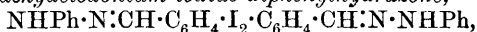
which it separates in white crystals on dilution with water, gives no coloration with ferric chloride, and when warmed with phenylhydrazine dissolves, but separates again unchanged on cooling.

These properties of ellagic acid agree with Graebe's formula for this substance (Abstr., 1903, i, 262). G. Y.

Di-*p*-benzaldehydeiodonium Hydroxide and its Derivatives.

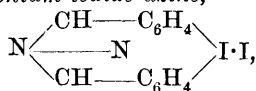
CONRAD WILLGERODT and HANS BOGEL (*Ber.*, 1905, **38**, 3446—3451).—*Di-p-benzaldehydeiodonium hydroxide*, $\text{COH}\cdot\text{C}_6\text{H}_4\cdot\text{I}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, prepared by the action of silver oxide on a mixture of iodoso- and iodoxy-benzaldehyde, is obtained as an uncrystallisable solid. The *chloride* crystallises in colourless needles and melts at 180° ; the *bromide* forms very minute, colourless needles and melts at 151° ; the *iodide* crystallises from water in golden-yellow needles and prisms and melts at 138° to a bright yellow liquid; the *periodide* forms black needles aggregated in rosettes and bunches, which, on heating, soften to a dark liquid at 102° . The *dichromate* is obtained as a reddish-yellow, crystalline powder which decomposes very rapidly. The *platinichloride* separates from dilute aqueous solutions in golden-yellow prisms and decomposes to a black liquid at 170° ; the *mercurichloride* forms colourless needles decomposing at 160 — 168° .

Di-p-benzaldehydeiodonium iodide diphenylhydrazone,



is obtained as a reddish-yellow, amorphous powder which decomposes at 115 — 125° to a red liquid. The *di-semicarbazone* crystallises from alcohol in almost colourless needles melting at 218° .

Di-p-benzaldehydeiodonium iodide azine,



prepared by the action of hydrazine sulphate on dibenzaldehydeiodonium iodide, separates as a yellow precipitate, insoluble in ordinary solvents, which begins to decompose about 200° .

The *benzidine* derivative, $\text{N} \begin{array}{c} \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 \\ \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{I}_2 \cdot \text{C}_6\text{H}_4 \\ \text{---} \text{N} \end{array} \text{CH}$, crystallises from nitrobenzene in yellow leaflets which decompose above 300° and become dark red when exposed for a long time to the atmosphere.

E. F. A.

p-Iodobenzaldehyde, *p*-Iodobenzophenone, and Derivatives of the Latter containing Polyvalent Iodine. CONRAD

WILLGERODT and HANS BOGEL (*Ber.*, 1905, **38**, 3451—3458).—*p*-Iodobenzaldehyde, prepared by the interaction of diazotised *p*-anhydroaminobenzaldehyde with potassium iodide, forms snow-white crystals melting at 78° ; *p*-iodobenzylideneaniline, $\text{C}_6\text{H}_4\text{I}\cdot\text{CH}\cdot\text{NPh}$, crystallises from alcohol in large, light yellow leaflets melting at 89 — 91° . *p*-Iodobenzophenone, $\text{C}_6\text{H}_4\text{I}\cdot\text{COPh}$ prepared by the interaction of iodobenzaldehyde with magnesium phenyl bromide, treatment of the resulting compound with water to form *p*-iodobenzhydrol, and subsequent oxidation of this with potassium dichromate, crystallises in well-formed, colourless needles melting at 100 — 101° .

p-Benzophenone iododichloride, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot ICl_2$, separates in faintly greenish-yellow, monoclinic plates and loses its chlorine above 90° . *p*-Iodosobenzophenone, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot IO$, is obtained as an amorphous, yellow or orange powder which sinters at 150° and is completely melted at 180° ; the acetate crystallises in long needles aggregated in bunches and melts at 168° .

p-Iodoxybenzophenone, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot IO_2$, is a colourless, odourless, sandy powder which explodes faintly when heated on platinum foil.

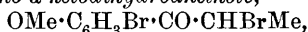
p-Benzophenone phenyliodonium hydroxide,



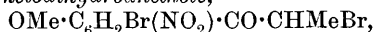
is obtained in the form of an alkaline, yellow solution by the interaction of benzophenone iododichloride and mercurydiphenyl and treatment of the resulting iodonium iodide with silver oxide and water. The chloride crystallises in colourless, glistening needles melting at about 200° ; the bromide forms small, colourless needles melting at 157° ; the iodide is sparingly soluble in water, separates in light yellow needles, and melts at 138° ; the dichromate crystallises in long, orange-yellow needles and decomposes above 120° . The platinichloride crystallises in small, yellow prisms and decomposes at 180° ; the mercurichloride crystallises in colourless needles and melts at 147 — 150° .

E. F. A.

Dibromides of Aromatic Propenyl Compounds. III. Behaviour of Anethole Dibromide and *iso*Safrole Dibromide on Oxidation. PAUL HOERING (*Ber.*, 1905, 38, 3458—3463. Compare *Abstr.*, 1904, i, 577; this vol., i, 592).—On oxidation of anethole dibromide with concentrated nitric acid in the cold, a colourless substance crystallising in needles and melting at 98 — 99° is obtained, and is probably β -*l*-dibromo- α -ketodihydroanethole,



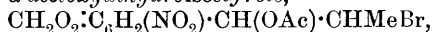
together with an oil which is a mixture of the above substance and β -*l*-dibromonitro- α -ketodihydroanethole,



melting at 92° . With chromic acid, in the main, the above bromoanethole ketobromide is obtained, mixed with anethole ketobromide; permanganate gives a similar result.

By the action of nitric acid on β -*l*-dibromo- α -methoxydihydroanethole, the above bromoanetholeketobromide is formed; from β -bromo- α -methoxydihydroanethole, the β -bromonitro- α -ketodihydroanethole, melting at 94 — 95° , mixed with some dinitro-compound, was obtained.

β -Bromonitro- α -acetoxydihydroisosafole,

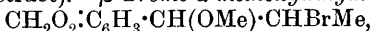


prepared by the action of nitric acid on *isosafole* dibromide in glacial acetic acid, forms yellow, prismatic needles melting at 113° ; nitroisosafoleoxide, $CH_2O_2 \cdot C_6H_2(NO_2) \cdot \langle \begin{smallmatrix} CH \\ O \end{smallmatrix} \rangle CHMe$, is formed on hydro-

lysis, and reacts with alcoholic potassium hydroxide to form a compound, melting at 134 — 135° , soluble in alkali hydroxides.

E. F. A.

Dibromides of Aromatic Propenyl Compounds. IV. Substitution in and Elimination of Bromine Atoms from Dibromides. PAUL HOERING (*Ber.*, 1905, **38**, 3464—3476. Compare preceding abstract).—*β*-Bromo-*α*-methoxydihydroisosafole,



is a colourless, strongly refractive oil boiling at 166—169° under 11 mm. and at 158—164° under 8 mm. pressure; the *α*-ethoxy-derivative is a colourless oil, which boils at 175—178° under 18 mm. and at 165—170° under 10 mm. pressure,

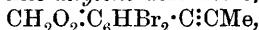
β-*η*-Tribromo-*α*-methoxydihydroisosafole,



forms large crystals melting at 111°; the corresponding *ethoxy*-derivative crystallises in plates melting at 89°. The *propenyl ether* of *isosafole*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C}(\text{OEt})\cdot\text{CHMe}$, prepared by the action of alcoholic alkali hydroxides on *β*-bromo-*α*-hydroxydihydroisosafole, boils at 143—145° under 10 mm. pressure. *β*-Bromo-*α*-hydroxydihydroisosafole and the corresponding dibromosafole, prepared by heating the corresponding dibromides with calcium carbonate and acetone, could only be obtained as oils. Similarly, by the action of sodium acetate in acetic acid solution on the dibromides, *β*-bromo-*α*-acetoxydihydroisosafole was obtained as a viscid oil, *β*-*η*-tribromo-*α*-acetoxydihydroisosafole forming a colourless, crystalline compound melting at 140—142°.

β-Bromo-*α*-acetoxypropylbenzene, $\text{OAc}\cdot\text{CHPh}\cdot\text{CHBrMe}$, is a colourless oil boiling at 142—145° under 11 mm. pressure and having a sp. gr. 1.388 at 19.5°.

Bromoisosafole dibromide, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CH}\cdot\text{CBrMe}$, formed by the action of sodium methoxide on bromoisosafole dibromide, melts at 65°. By the action of alcoholic potassium hydroxide on the dibromide, the *allylene* derivative, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{C}\cdot\text{CMe}$, melting at 56—59°, is formed. By the action of sodium methoxide on dibromoisosafole dibromide, a *compound*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{HBr}_2\cdot\text{CH}\cdot\text{CBrMe}$, melting at 153—154° is formed. The *allylene* derivative,



crystallises in colourless needles melting at 180—181°. In carbon disulphide solution, it unites with two atoms of bromine, forming a *compound* melting at 126—128°. E. F. A.

Dibromides of Aromatic Propenyl Compounds. V. Oxides of Propenyl Compounds and their Reactions. PAUL HOERING (*Ber.*, 1905, **38**, 3477—3486. Compare preceding abstracts).—Anethole oxide (this vol., i, 593) has a sp. gr. 1.0637 at 17°. Anisylacetone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, has a sp. gr. 1.0707 at 17°; it yields two isomeric *oximes* crystallising in long, colourless needles and melting at 61—62° and 78—79° respectively.

isoSafrole oxide has a sp. gr. 1.2128 at 17°. *Piperonylacetone*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{COMe}$, boils at 149—151° under 10 mm. pressure and at 283—284° under 760 mm. pressure. The colourless, almost odourless oil has a sp. gr. 1.2017 at 17.5°; the *oxime* separates in needles melting at 87—88°.

β-Bromoanethole oxide is obtained as an oil boiling between 175° and 185° under 18 mm. pressure. *Bromoisosafrole β-ketone* yields two isomeric oximes melting at 147—149° and 95° respectively. *Dibromoisosafrole ketone* forms a poorly-defined *oxime* melting at 144—150°.

Both *isosafrole oxide* and *bromoisosafrole oxide* form liquid additive compounds with 1 mol. of acetic acid; the *bromoisosafrole glycol*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{OH}$, obtained by the action of alcoholic alkali hydroxide on the latter, forms a crystalline compound melting at 107—109°. *Dibromoisosafrole glycol β-acetate*, prepared by warming *dibromoisosafrole oxide* with acetic acid, melts at 186—190°; the corresponding *glycol* forms pale yellow plates melting at 154—155°.

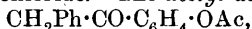
β-?-Tribromo-α-hydroxydihydroisosafrole forms a *chlorobromide*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{HBr}_2\cdot\text{CHCl}\cdot\text{CHBrMe}$, melting at 105—107°. *α-?-Dibromoisosafrole β-acetate*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CHBr}\cdot\text{CHMe}\cdot\text{OAc}$, prepared either by heating *bromoisosafrole glycol β-acetate* with hydrogen bromide or by the addition of acetyl bromide to *bromoisosafrole oxide*, separates from petroleum in colourless crystals melting at 128—132°; the corresponding *tribromoisosafrole-β-acetate* melts at 128—130°.

By the action of hydrogen bromide on *isosafrole oxide* in benzene solution, a colourless, crystalline compound, $\text{C}_{20}\text{H}_{18}\text{O}_5$, melting at 240—241°, was obtained. From *bromoisosafrole oxide*, *α-?-dibromo-β-hydroxydihydroisosafrole*, a clear, viscid oil which rapidly decomposed, was obtained. *α-?-Dibromo-β-hydroxydihydrodiisosafole*,

$\text{CH}_2\text{O}_2\cdot\text{C}_6\text{HBr}_2\cdot\text{CH}(\text{OH})\cdot\text{CHBrMe}$,
melts at 121—123°.

E. F. A.

p-Hydroxydeoxybenzoin. SIEGMUND WEISL (*Monatsh.*, 1905, 26, 977—1002. Nencki, *Abstr.*, 1881, 591, 811; Rasinski, *Abstr.*, 1882, 1288).—*p-Hydroxydeoxybenzoin*, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, can be prepared by adding zinc chloride to a boiling mixture of phenylacetic acid and phenol and heating at 170—200°, or by the action of aluminium chloride on phenylacetyl chloride and phenol in nitrobenzene solution at 80° (compare Graebe and Bungener, *Abstr.*, 1879, 790; Behn, D.R.-P. 95901). It crystallises from water in yellowish-red, feathery aggregates, melts at 142° (corr.), is easily soluble in glacial acetic acid, alcohol, ether, benzene, or aqueous alkali hydroxide, but only sparingly so in hot water, and gives a characteristic, dark brown coloration with aqueous-alcoholic ferric chloride. The *acetyl* derivative,



crystallises from dilute alcohol in small, slightly yellow plates and melts at 82° (corr.). The *oxime*, $\text{C}_{14}\text{H}_{13}\text{O}_2\text{N}$, formed by Meyer and Oelkers' method (*Abstr.*, 1888, 703), separates from its aqueous-alcoholic solution in glistening, yellowish-white crystals and melts at 85° (corr.).

When boiled with 70 per cent. aqueous potassium hydroxide, *p-hydroxydeoxybenzoin* is decomposed with formation of toluene and *p-hydroxybenzoic acid*.

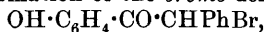
p-Hydroxybenzil, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COPh}$, is formed by oxidation of *p-hydroxydeoxybenzoin* with chromic acid in boiling glacial acetic acid

solution, crystallises slowly from its cold concentrated alcoholic solution, to which water has been added, in small, orange needles, and melts at 175° (corr.). With solid potassium hydroxide in concentrated alcoholic solution, it gives a dark red coloration, which disappears on warming.

The *hydrochloride* of the *dioxime*, $C_{14}H_{12}O_3N_2 \cdot 2HCl$, crystallises from absolute alcohol in white, prismatic needles and melts and decomposes at 155° (corr.).

When reduced with sodium amalgam in boiling alcoholic solution, *p*-hydroxydeoxybenzoin yields a *product* which has the empirical formula $C_{29}H_{27}O_3$, crystallises from alcohol in small leaflets, and melts at 165° (corr.).

The action of bromine on *p*-hydroxydeoxybenzoin in glacial acetic acid solution leads to the formation of the *bromo-derivative*,

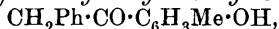


which crystallises from dilute alcohol, melts at 108° (corr.), and forms silver bromide when treated with silver nitrate in cold aqueous-alcoholic solution. The *iodo-derivative*, $OH \cdot C_6H_4 \cdot CO \cdot CHPhI$, formed by adding a solution of iodine in potassium iodide to a boiling aqueous solution of *p*-hydroxydeoxybenzoin and borax, crystallises slowly from alcohol in aggregates of rose-coloured, glistening needles, melts at 195° (corr.), and is easily soluble in warm alcohol, ether, or glacial acetic acid.

Phenyl phenylacetate, $CH_2Ph \cdot CO_2Ph$, is prepared by treating a mixture of phenylacetic acid and phenol with phosphoric oxide in boiling chloroform solution. It is obtained on evaporation of its ethereal solution in nodular aggregates or white crystals, melts at 35° (corr.), and is easily soluble in alcohol, glacial acetic acid, or light petroleum. When boiled with aqueous potassium hydroxide of sp. gr. 1.2, the ester is hydrolysed with formation of phenylacetic acid and phenol.

G. Y.

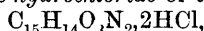
***p*-Hydroxymethyldeoxybenzoins.** EDMUND BLAU (*Monatsh.*, 1905, 26, 1149—1164).—4-Hydroxy-3-methyldeoxybenzoin,



is formed by adding zinc chloride to a mixture of phenylacetic acid and *o*-cresol heated at 180 — 200° in a reflux apparatus or by the action of aluminium chloride on phenylacetyl chloride and *o*-cresol dissolved in nitrobenzene. It crystallises from hot water in slightly yellow or red, feathery, crystalline aggregates, melts at 152° , is easily soluble in aqueous alkali hydroxides, alcohol, ether, or benzene, and gives a characteristic brown coloration with aqueous ferric chloride. When boiled with 70 per cent. aqueous potassium hydroxide in a reflux apparatus, it is decomposed with formation of toluene and 6-hydroxy-*m*-toluic acid. The *acetyl* derivative, $CH_2Ph \cdot CH_2 \cdot CO \cdot C_6H_3Me \cdot OAc$, crystallises from dilute alcohol in glistening, white needles and melts at 73° . The *oxime*, $C_{15}H_{14}O \cdot N \cdot OH$, crystallises in quadratic leaflets or white needles and melts at 158° .

4-Hydroxy-3-methylbenzil, $CH_2Ph \cdot CO \cdot CO \cdot C_6H_3Me \cdot OH$, is formed by the oxidation of 4-hydroxy-3-methyldeoxybenzoin with chromic oxide in

boiling glacial acetic acid solution; it separates from dilute acetic acid as a yellow, flocculent precipitate, melts at 182—183°, or when boiled with water, and gives a dark red coloration with potassium hydroxide in alcoholic solution. The *hydrochloride* of the *dioxime*,



crystallises from alcohol in long, white needles and melts at 149°.

When reduced with sodium amalgam in alcoholic solution, 4-hydroxy-3-methyldeoxybenzoin yields a *product*, $\text{C}_{31}\text{H}_{32}\text{O}_3$, which separates from alcohol as a white, flocculent precipitate and melts at 117°. *Bromo-4-hydroxy-3-methyldeoxybenzoin*, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$, is formed by the action of bromine on 4-hydroxy-3-methyldeoxybenzoin in glacial acetic acid solution at 80°; it crystallises from dilute alcohol and melts at 132°. *Iodo-4-hydroxy-3-methyldeoxybenzoin*, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{I}$, formed by the action of iodine in potassium iodide solution on 4-hydroxy-3-methyldeoxybenzoin in presence of sodium borate, crystallises in concentric aggregates of glistening needles and melts at 120°. These bromo- and iodo-compounds yield the silver haloids when treated with silver nitrate in aqueous-alcoholic solution.

4-Hydroxy-2-methyldeoxybenzoin, $\text{CH}_2\text{Ph} \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$, is formed by the condensation of *m*-cresol and phenylacetic acid in presence of zinc chloride at 200°; it melts at 142°, is soluble in hot water, alcohol, or glacial acetic acid, and yields toluene and 4-hydroxy-*o*-toluic acid when boiled with 70 per cent. aqueous potassium hydroxide.

G. Y.

Dihydroxydeoxybenzoin. FRIEDRICH FINZI (*Monatsh.*, 1905, 26, 1119—1138. Compare Bülow and Grotowsky, *Abstr.*, 1902, i, 554).—1-*m*-Dihydroxydeoxybenzoin (dihydroxyphenyl benzyl ketone), $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ [$(\text{OH})_2 = 2:4$ or $2:6$], is formed by heating phenylacetic acid and resorcinol in molecular amounts, with zinc chloride, not above 150°, or by adding aluminium chloride to a solution of molecular amounts of phenylacetyl chloride and resorcinol in nitrobenzene at 70—80°. It crystallises from much boiling water in thin, glistening leaflets, melts at 104° (corr.), is soluble in most organic solvents, aqueous alkali hydroxides, or, without evolution of carbon dioxide, in sodium carbonate solution, and with ferric chloride in aqueous or alcoholic solution gives a dark violet coloration, which disappears on addition of sodium carbonate. It is identical, probably, with Bülow and Grotowsky's product (*loc. cit.*). When treated with acetyl chloride in pyridine solution, dihydroxydeoxybenzoin forms the *diacetyl* derivative, $\text{C}_{14}\text{H}_{10}\text{O}_3\text{Ac}_2$, which crystallises from alcohol in slender, white needles, melts at 107° (corr.), and is easily soluble in concentrated sulphuric acid, acetone, chloroform, or benzene at the laboratory temperature. The *oxime*, $\text{C}_{14}\text{H}_{12}\text{O}_2 \cdot \text{N} \cdot \text{OH}$, crystallises in slender, yellow needles, sinters at 110°, and melts partially at 170°.

1-*m*-*Dihydroxybenzil*, $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CO} \cdot \text{COPh}$ [$(\text{OH})_2 = 2:4$ or $2:6$], is obtained in a yield of 15 per cent. of the theoretical by oxidising dihydroxydeoxybenzoin with an excess of potassium permanganate in dilute aqueous alkali carbonate solution, or in an almost theoretical yield by oxidation with boiling Fehling's solution. On addition to water of its solution in glacial acetic acid, it separates as a brown,

amorphous substance which sinters at 137° , melts at 239° , and is insoluble in water or light petroleum, but dissolves readily in alcohol, ether, or glacial acetic acid. The *hydrochloride* of the *dioxime*, $C_{14}H_{12}O_4N_2 \cdot 2HCl$, crystallises in long, colourless needles and melts at $155-156^{\circ}$.

Reduction of 1-*m*-dihydroxydeoxybenzoin, by means of sodium amalgam in boiling alcoholic solution through which a current of carbon dioxide is passed, leads to the formation of an amorphous, brown *product*, $C_{22}H_{18}O_4$, which is easily soluble in alcohol, ether, or acetone.

3 : 4-*Dihydroxydeoxybenzoin* (3 : 4-*dihydroxyphenyl benzyl ketone*), formed by adding zinc chloride to a mixture of phenylacetic acid and catechol at $140-150^{\circ}$, or by the action of aluminium chloride on a mixture of phenylacetyl chloride and catechol, crystallises from water in small, brown needles, melts at 173° , and with alcoholic ferric chloride gives a green coloration which becomes violet on addition of ammonia. When heated with 70 per cent. aqueous potassium hydroxide at 180° , it is decomposed with formation of toluene and 3 : 4-dihydroxybenzoic acid. The *diacetyl* derivative, $C_{18}H_{16}O_7$, crystallises from aqueous alcohol in glistening, white needles and melts at 105° (corr.).

2 : 5-*Dihydroxydeoxybenzoin* (2 : 5-*dihydroxyphenyl benzyl ketone*), formed by heating phenylacetic acid and quinol with zinc chloride at 150° , or by the action of aluminium chloride on a mixture of phenylacetyl chloride and quinol, crystallises in needles and melts at 170° . G. Y.

Certain Derivatives of Tetrabromo-*o*-benzoquinone. C. LORING JACKSON and H. A. CARLTON (*Amer. Chem. J.*, 1905, **34**, 422—441. Compare Jackson and Porter, *Abstr.*, 1904, i, 254).—The red compound, $4C_6O_2Br_4 \cdot MeOH$, formed as the first product of the action of methyl alcohol on tetrabromo-*o*-benzoquinone, can also be obtained by the action of tetrabromo-*o*-benzoquinone on the α -compound, $2C_6O_2Br_4 \cdot MeOH$. When either the red compound or the α -compound is warmed with dilute sodium hydroxide, the β -compound,

$2C_6O_2Br_4 \cdot MeOH$, is produced. By similar treatment, the α -benzyl compound is converted into the corresponding β -compound.

Both α - and β -compounds have been obtained with ethyl alcohol, *n*-propyl alcohol, and *isoamyl* alcohol. The following is a list of these compounds with their decomposition or melting points : $2C_6O_2Br_4 \cdot EtOH$, α -compound, $180-185^{\circ}$, β -compound, 228° ; $2C_6O_2Br_4 \cdot Pr^aOH$, α -compound, 180° , β -compound, 176° ; $2C_6O_2Br_4 \cdot C_5H_{11} \cdot OH$, α -compound, 150° , β -compound, 177° ; $2C_6O_2Br_4 \cdot CH_2Ph \cdot OH$, α -compound, $165-170^{\circ}$, β -compound, $216-217^{\circ}$. The α -*isoamyl* compound melts without becoming red, but when heated to 190° it is converted, like the other α -compounds, into hexabromo-*o*-quinocatechol ether. *tert*.-Butyl alcohol also appears to yield an α -compound, but the product was not obtained in the pure state.

When the water, methyl alcohol, and benzyl alcohol α -compounds are reduced with zinc and acetic acid, they all yield the same product

melting at 274—275°. This compound has not the composition assigned to it by Jackson and Porter (*loc. cit.*), but is probably represented by the formula $C_6Br_4 \cdot O_2 \cdot C_6H(OH)_2 \cdot O \cdot C_6Br_4 \cdot OH$; its *diacetyl* derivative melts at 304—305°, and its *triacetyl* derivative melts at 273—275°; the *tribenzoyl* derivative melts at 250—255°. When this reduction product is treated with nitric acid, it is converted into a mixture of two *substances*, one of which crystallises in small, red prisms and melts at 275—280°, whilst the other forms orange needles and does not melt below 310°. If the crude reduction product is boiled with alcohol or benzene, a *substance* is produced which has a pale lilac colour, becomes brown at about 200°, and does not melt below 310°; this substance cannot be obtained from the pure reduction product.

The *acetyl* derivative of the benzyl alcohol β -compound, $2C_6O_2Br_4 \cdot CH_2Ph \cdot OAc$, crystallises in small, white needles and melts at 210°. If the action of acetic anhydride is continued for six hours, a dark, charred mass is obtained, from which a mixture of benzene and methyl alcohol extracts a *substance* crystallising in brown needles and melting at 190—195°. E. G.

Additive Compounds of Quinones and Tertiary Amines. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1905, **34**, 441—459).—By the action of dimethylaniline on quinones, unstable additive compounds are produced. The following compounds have been prepared. The additive *compound* of tetrabromo-*o*-quinone, $C_6O_2Br_4 \cdot C_6H_5 \cdot NMe_2$, forms lustrous, purple needles which undergo rapid decomposition. Tetrachloro-*o*-benzoquinone yields a similar but even less stable product. Tetrachloro-*p*-benzoquinone yields a *compound*, $C_6O_2Cl_4 \cdot C_6H_5 \cdot NMe_2$, which crystallises in slender, deep blue prisms, melts at 105°, and decomposes rapidly on exposure to the air; when heated above its melting point, it is converted into the dark blue substance first described by Greiff (*Abstr.*, 1880, 41). Trichloro-*p*-benzoquinone furnishes a *compound*, $C_6HO_2Cl_3 \cdot C_6H_5 \cdot NMe_2$, which crystallises in slender, dark blue prisms, melts at 65°, and is soluble in ether, benzene, or acetone. The additive *compound* with 2 : 5-dichloro-*p*-benzoquinone crystallises in slender, deep blue needles. Chloroquinone and quinone yield dark red products with dimethylaniline from which a solid substance could not be isolated. The additive compound of tetrabromo-*p*-benzoquinone, $C_6O_2Br_4 \cdot C_6H_5 \cdot NMe_2$, forms purple, microscopic needles and melts at 65—68°. Trichlorotoluquinone gives a *compound*, $C_6MeO_2Cl_3 \cdot C_6H_5 \cdot NMe_2$, which crystallises in flat, purple prisms, melts at 68—73°, and is soluble in alcohol, benzene, or acetone. Toluquinone, dibromothymoquinone, dichlorodiethoxyquinone, 1 : 4-naphthaquinone and anthraquinone were found to unite with dimethylaniline to form coloured products from which no solid substance could be isolated. Quinone dibromide and quinone tetrabromide give a blue coloration with dimethylaniline. *p*-Quinoneoxime and 2 : 5-dichloroquinoneoxime give a red coloration with dimethylaniline, but the corresponding dioximes yield no coloration. The following compounds give no change of colour when treated with dimethylaniline. *p*-Diketocyclohexene, dichlorodimethoxyquinone

dibenzoyldimethylacetal, dichlorodiethoxyquinone tetraethylacetal, dichlorodiisoamyloxyquinone, dichlorodiphenoxyquinone, dianilino-bromoquinoneanil, tetrachloroquinol, dichlorodiisoamyloxyquinol, and dichlorodibenzyloxyquinol.

Coloured products are formed by the action of *p*-bromodimethylaniline and of dibromodimethylaniline on quinone and trichloroquinone. The hydrobromide of dibromodimethylaniline gives a slight red coloration with trichloroquinone due to partial dissociation of the salt. Neither phenyltrimethylammonium bromide nor iodide gives any coloration with quinone or trichloroquinone.

The additive compound, $C_6O_2Cl_4 \cdot C_6H_4Me \cdot NMe_2$, obtained by the union of tetrachloro-*p*-benzoquinone and dimethyl-*p*-toluidine, forms blue crystals, melts at 114° , is sparingly soluble in alcohol or acetone, and is unstable in the air. The compound, $C_6HO_2Cl_3 \cdot C_6H_4Me \cdot NMe_2$, from trichloroquinone and dimethyl-*p*-toluidine, crystallises in long, blue needles. Coloured products are also formed by the action of dimethyl-*p*-toluidine on 2:5-dichloroquinone, chloroquinone, and quinone. The additive compound, $C_6MeO_2Cl_3 \cdot C_6H_4Me \cdot NMe_2$, from trichlorotoluquinone and dimethyl-*p*-toluidine, crystallises in deep blue needles and melts at $74-76^\circ$. The compound,



from tetrabromo-*p*-benzoquinone, forms pale blue crystals and melts at 109° .

The action of dimethyl-*o*-toluidine, benzyldimethylamine, dimethyl-isoamylamine, α -naphthyldimethylamine, α -naphthyldiethylamine, β -naphthyldiethylamine, α -naphthylamine, diphenylamine, pyridine, methylaniline, and tetramethyldiaminotriphenylmethane on various quinones has been studied and the results are described; in every case a coloured product is obtained.

The probable constitution of these additive compounds is discussed.

E. G.

Preparation of 2-Hydroxy-1:4-naphthaquinone. HERBERT TEICHNER and HUGO WEIL (*Ber.*, 1905, **38**, 3376—3377).—2-Hydroxy-1:4-naphthaquinone is easily prepared by adding a cold mixture of hydrogen peroxide and aqueous sodium hydroxide to 1:2-naphthaquinone suspended in water. Sodium 1:2-naphthaquinone-6-sulphonate is oxidised in a similar manner to sodium 2-hydroxy-1:4-naphthaquinone-6-sulphonate; but sodium 1:2-naphthaquinone-3:6-disulphonate cannot be converted into the corresponding derivative of α -naphthaquinone.

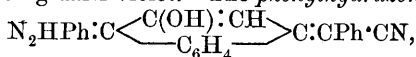
W. A. D.

Condensations with 1:2-Naphthaquinone-4-sulphonic Acid. FRANZ SACHS and MARIO CRAVERI (*Ber.*, 1905, **38**, 3685—3696. Compare Ehrlich and Herter, *Abstr.*, 1904, i, 598).—2-Hydroxy-1:4-naphtha-

quinone-4-phenylcyanomethide, $CO \langle \begin{smallmatrix} C(OH) \cdot CH \\ C_6H_4 \end{smallmatrix} \rangle C : CPh \cdot CN$, prepared

by the interaction of sodium naphthaquinone sulphonate with benzyl cyanide, crystallises in yellow needles melting at 201° and gives a red coloration with alcoholic sodium hydroxide, the solution in concentrated

sulphuric acid being dark violet. The *phenylhydrazone*,



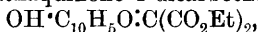
crystallises in cherry-red leaflets melting at 250° ; it gives with sulphuric acid a dark cherry-red, and with alkaline hydroxides an orange-yellow coloration. The *ethyl ether*, $\text{OEt}\cdot\text{C}_{10}\text{H}_5\text{O}\cdot\text{CPh}\cdot\text{CN}$, separates in yellow rods melting at $163\text{--}165^\circ$; the *methyl ether* forms yellow needles, which melt at 190° . 2-Methoxy-4-cyanobenzyl-*a-naphthol*, $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{OMe})\cdot\text{CHPh}\cdot\text{CN}$, prepared by reducing the methyl ether with zinc dust and acetic acid, crystallises in colourless, star-shaped needles or prisms melting at 195° ; the *acetate* separates in colourless prisms and melts at $167\text{--}168^\circ$.

1 : 2-Diacetoxy-4-cyanobenzyl*naphthalene*, $\text{C}_{10}\text{H}_5(\text{OAc})_2\cdot\text{CHPh}\cdot\text{CN}$, formed by the direct reduction of the hydroxynaphthaquinone with zinc dust and acetic acid in presence of sodium acetate and acetic anhydride, forms colourless prisms melting at $153\text{--}155^\circ$.

4-Cyanobenzyl-1 : 2-naphthaquinol, $\text{C}_{10}\text{H}_5(\text{OH})_2\cdot\text{CHPh}\cdot\text{CN}$, is obtained in the form of colourless, narrow plates or rhombic cubes melting at 235° . When condensed with *o*-phenylenediamine, hydroxynaphthaquinonephenylcyanomethide yields a compound melting at 228° and crystallising in light yellow needles, which dissolve in sulphuric acid with a dark bordeaux-red and in alcoholic alkaline hydroxides with a green coloration.

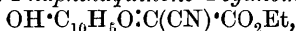
2-Hydroxy-1 : 4-naphthaquinone-4-*p*-nitrophenylcyanomethide, prepared from *p*-nitrobenzyl cyanide and the sulphonic acid, is a yellow powder melting at 220° and possessing electrical properties; the *methyl ether* crystallises in yellow rods or needles melting at 243° , whilst the condensation product with *o*-phenylenediamine separates in greenish-yellow rods, which melt at $212\text{--}214^\circ$ and dissolve in alcoholic alkali hydroxides with a blue coloration.

2-Hydroxy-1 : 4-naphthaquinone-4-dicarbethoxymethide,



obtained on condensing the sulphonate with ethyl malonate, crystallises in thick, yellow needles melting at $110\text{--}112^\circ$, and is identical with the compound described by Liebermann (Abstr., 1899, i, 373).

Ethyl 2-hydroxy-1 : 4-naphthaquinone-4-cyanomethidecarboxylate,



crystallises in yellow rods melting at 130° and gives a reddish-yellow coloration with sulphuric acid. The *oxime* crystallises in brownish-yellow rods melting at 236° . With *o*-phenylenediamine, a compound, $\text{C}_{21}\text{H}_{15}\text{O}_2\text{N}_3$, is obtained which melts at $156\text{--}159^\circ$ and crystallises in small, yellow bundles of needles. 2-Hydroxy-1 : 4-naphthaquinone-4-dicyanomethide forms yellow needles, melting at 213° , and gives a dark reddish-yellow solution in sulphuric acid. E. F. A.

2-Bromo-*a*-aminoanthraquinone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 160169).—Finely-divided *a*-aminoanthraquinone, prepared by precipitating its solution in sulphuric acid with water, is suspended in glacial acetic acid and the calculated quantity of bromine added. After boiling and again cooling, 2-bromo-*a*-aminoanthraquinone separates in rosettes of yellowish-red needles. It melts at $180\text{--}181^\circ$

and is insoluble in water, but dissolves readily in hot glacial acetic acid, aniline, or pyridine, sparingly in alcohol or ether. The solution in concentrated sulphuric acid is yellow, that in acid containing 40 per cent. anhydride is bluish-violet.

2-Bromo-5-nitro- α -aminoanthraquinone, prepared in similar manner from 5-nitro- α -aminoanthraquinone, forms reddish-brown needles and melts at 240—245°.

C. H. D.

Elimination of the Sulpho-group from Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 160104. Compare Abstr., 1904, i, 513; this vol., i, 361).—It has been shown that the sulphonation of anthraquinone and its derivatives in the α -position takes place most readily in the presence of a mercury salt. It is now found that the elimination of the α -sulpho-group, which is only incomplete on heating with dilute sulphuric acid, is rendered complete by the addition of a mercury salt. In this way, anthraquinone is obtained from either anthraquinone- α -sulphonic acid or anthraquinone-1 : 5- or -1 : 8-disulphonic acid.

C. H. D.

Chrysophanic Acid. OTTO A. OESTERLE (*Arch. Pharm.*, 1905, 243, 434—442).—Chrysophanic acid was prepared from chrysarobin by oxidation in alkaline solution and fractional crystallisation from benzene. The fraction of highest melting point melted at 186° and still contained methoxyl; it was freed from methoxyl by heating it in benzene solution with aluminium chloride (hydriodic acid effects reduction to the hydroanthranone at the same time that it removes methoxyl). *Chrysophanic acid*, $C_{15}H_{10}O_4 = C_{15}H_8O_2(OH)_2$, when free from methoxyl, crystallises in brownish-yellow plates which melt at 196°; its pale yellow *diacetyl* derivative melts at 208°.

Chrysophanic acid cannot be methylated with methyl iodide. But when a solution of the crude acid in aqueous potassium hydroxide is shaken with methyl sulphate, and the solid which separates is extracted with boiling dilute aqueous sodium hydroxide, the insoluble residue contains the *dimethyl ether* of chrysophanic acid, $C_{15}H_8O_2(OMe)_2$, which crystallises in orange-yellow needles melting at 195°, mixed with a small quantity of another yellow substance melting at 224° (probably a trimethoxymethylanthraquinone), which lowers its melting point and is very difficult to separate from it. The alkaline extract contains unchanged chrysophanic acid together with its *monomethyl ether*; the latter can be precipitated by saturating the solution with carbon dioxide; it crystallises in orange needles, which melt at 204° and form a lemon-yellow *acetyl* derivative melting at 204—205°.

C. F. B.

Resin Oil of Pinus Longifolia. FRANK RABAK (*Chem. Centr.*, 1905, ii, 896—897; from *Pharm. Rev.*, 23, 229—232).—The resin oil prepared from *Pinus longifolia*, which is indigenous to the lower Himalayas, forms a white, rather tough, opaque mass and has a granular structure which is probably due to partial crystallisation of the resin acid. Its odour is extremely pleasant and somewhat resembles that of limonene. It has a sp. gr. 0.990, $[\alpha]_D - 7.42^\circ$, acid number 129, ester number 11, and saponification number 140. When distilled with steam it yields about 18.5 per cent. of a volatile oil which has the characteristic odour

of pinene and a somewhat fainter odour of limonene. The oil has a sp. gr. 0.866 and $[\alpha]_D + 2.48'$. When fractionally distilled, it yields (1) 56 per cent. of a liquid which boils at $165-170^\circ$ and has $[\alpha]_D - 2^\circ$; (2) 20 per cent. which boils at $170-175^\circ$ and has $[\alpha]_D + 2.48'$; (3) 9 per cent. which boils at $175-180^\circ$ and has $[\alpha]_D + 6.50'$; and (4) 15 per cent. which boils at 180° and above and has $[\alpha]_D + 18.12'$. The oil probably contains *l*-pinene together with a small quantity of *d*-limonene. The presence of pinene was detected in the first fraction by means of amyl nitrite, but a crystalline nitrosochloride was not isolated. Attempts to prepare the hydrochloride and bromine additive compound also failed. The white, crumbly resin which remains after distilling the oil has acid number 142, ester number 13, and saponification number 155; a 10 per cent. solution in a 100 mm. tube has $\alpha_D = 1.10'$. Crystals of a resin acid melting at $138-140^\circ$ separate from the solution of the resin in glacial acetic acid after remaining for 24 hours.

E. W. W.

The Cyanogenetic Glucosides in the Leaves of the Cherry-laurel (*Prunus Laurocerasus*) and in the Bark of the Bird-cherry (*P. Padus*). KARL JOUCK (*Arch. Pharm.*, 1905, 243, 421-426).—A yellow, amorphous, very hygroscopic glucoside was isolated from the bark of *Prunus padus* by a method described in detail in the paper, the yield being 0.5 per cent. It contained C 53.6, H 6.8, N 2.84 per cent.; it yielded 6.1 per cent. of hydrocyanic acid and 38.9 of dextrose when hydrolysed with emulsin, and an acid was obtained from it analogous with amygdalic acid and forming a barium salt which contained C 40.5, H 5.6, Ba 16.5 per cent.

From the leaves of *P. laurocerasus*, a similar glucoside was isolated in a similar manner; the yield was 0.8 per cent. It contained C 54.3, H 6.8, N 1.54 per cent.; it yielded 2.75 per cent. of hydrocyanic acid and 27.2 of dextrose when hydrolysed, and the crystalline barium salt of the acid obtained from it analogous to amygdalic acid contained C 42.1, H 5.4, Ba 14.2 per cent.

C. F. B.

Sambunigrin, a New Cyanogenetic Glucoside obtained from the Leaves of *Sambucus Nigra*. ÉMILE BOURQUELOT and ÉMILE DANJOU (*Compt. rend.*, 1905, 141, 598-600; *J. Pharm. Chim.*, [vi], 22, 385-391. Compare this vol., ii, 605, and Guignard, this vol., ii, 604).—The leaves of *Sambucus nigra* contain only traces of emulsin; it is therefore possible to extract from the air-dried or the fresh leaves the glucoside *sambunigrin*, $C_{14}H_{17}O_6N$, which crystallises from ethyl acetate in long, colourless needles, sinters at 149° , and melts at $151-152^\circ$, has $[\alpha]_D - 76.3^\circ$, is readily soluble in water or ethyl alcohol, less soluble in ethyl acetate, and almost insoluble in ethyl ether; it has a sweet taste at first, afterwards becoming bitter. On hydrolysis by means of emulsin, sambunigrin yields dextrose, hydrogen cyanide, and benzaldehyde, and is therefore an isomeride of Fischer's amygdonitrile glucoside, $C_{14}H_{17}O_6N$, from which it differs by its strong levorotatory power -76.3° instead of -26.1° .

M. A. W.

Aloes. ALEXANDER TSCHIRCH and O. HOFFBAUER (*Arch. Pharm.*, 1905, 243, 399—420).—From Zanzibar aloes, an *aloin* could not be obtained satisfactorily by means of lime or of chloroform and methyl alcohol. It was found best to allow the powdered drug to remain for several days with an equal weight of alcohol, the mixture being shaken occasionally, and then to recrystallise the insoluble portion (*zanaloin*) from dilute alcohol. *isoAloin* is not present. From Jaferabad, Barbadoes, and Curaçoa aloes, the aloins (*jafaloin*, *barbaloin*, and *curaloin*) could be obtained by extracting with methyl alcohol and freeing the extract from resin by precipitation with chloroform. *Barbaloin* and *curaloin* are identical, with melting point 147° and composition $C_{16}H_{16}O_7$. *Capaloin*, from *Aloe lucida*, and the *aloin* of the Uganda aloe are also identical, with melting point 147° but composition $C_{16}H_{18}O_7$; *zanaloin* also has this composition, but melts at 212° . *Jafaloin*, melting at 152° and containing C 60.5, H 5.5 per cent., and *nataloin* are distinct individuals. The aloes from the Barbadoes contained but little *isoaloin*, and those from Jaferabad contained none, whilst those from Curaçoa contained a considerable quantity.

Aloin-reds were isolated from Natal and Curaçoa aloes, in very small amount in the latter case. The former has the composition, $C_{16}H_{16}O_8$, of an oxidation product of *nataloin*; it does not yield chrysamic acid when heated with concentrated nitric acid, whereas *curaloin-red* does. The solubilities and absorption spectra of several *aloin-reds* are described.

From Curaçoa aloes, an *anthraglucoside* was isolated, which, by boiling with 1 per cent. sulphuric acid, was hydrolysed to *emodin* and a sugar, of which the phenylosazone melted at 183° (compare Leger, *Abstr.*, 1904, i, 907).

When hydrolysed with boiling 10 per cent. sulphuric acid, the *resin* of Zanzibar aloes yields *p*-coumaric acid, and that of Curaçoa aloes cinnamic acid, whilst the corresponding acid product from Jaferabad aloes could not be isolated; in all cases, a *resinotannol* was obtained also. All these *resinotannols* yield *picric* and *oxalic* acids when heated with nitric acid of sp. gr. 1.27. *Barb-* and *cur-aloresinotannols* have the composition $C_{22}H_{26}O_6$; *zanaloresinotannol* is $C_{22}H_{22}O_8$, isomeric with *cap-* and *nat-aloresinotannol*; whilst *jafaloresinotannol* is $C_{20}H_{18}O_6$, isomeric with *feroaloresinotannol*. Accompanying *jafaloresinotannol* is a substance which is soluble in water and yields a little chrysamic acid when oxidised with nitric acid. C. F. B.

Red Sulphur Dyes from Resorcinol. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 160395).—Red dyes are obtained when resorcinol is fused with sulphur and an aromatic formyl compound such as formanilide, with or without the addition of glycerol as a solvent, at 180 — 185° . The products are dark red, insoluble in water, and dissolve in sodium sulphide to red solutions. C. H. D.

Yellow Sulphur Dye. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 159725).—A fast yellow dye, soluble in sodium sulphide, is obtained on fusing 2:4-diaminophenyl thiocyanate with sulphur at 140 — 240° . C. H. D.

Constitution of Tannin. MAXIMILIAN NIERENSTEIN (*Ber.*, 1905, 38, 3641—3642).—In agreement with the usual supposition that tannin is a digallic acid, $C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_2(OH)_2 \cdot CO_2H$, it is shown that when distilled with zinc dust it yields diphenylmethane, just as compounds of the type $\begin{array}{c} C_6H_4 \cdot CO \\ C_6H_4 \cdot O \end{array}$ yield fluoran (Graebe, *Abstr.*, 1903, i, 262; A. G. Perkin and Nierenstein, *Trans.*, 1905, 87, 1412). J. J. S.

Bromo-derivatives of 4-Pyrone and the Stability of Halogen Derivatives of 2- and 4-Pyrones. FRANZ FEIST and ERICH BAUM (*Ber.*, 1905, 38, 3562—3574. Compare Feist, *Abstr.*, 1892, 587; 1893, i, 403; Feist and Molz, *Abstr.*, 1899, i, 675; Peratoner and Castellana, *this vol.*, i, 806; Peratoner and Tamburello, *ibid.*, 807).—The action of a large excess of bromine on 4-pyrone in presence of a small quantity of iodine, ferric chloride, or phosphorus leads to the formation of a *perbromide*; this is obtained as a yellow, crystalline powder, and when treated with boiling water decomposes with formation of (1) 3:5-dibromo-4-pyrone, $O \begin{array}{c} \text{CH:CB}r \\ \text{CH:CB}r \end{array} CO$, which crystallises from ether in prisms, or from water or light petroleum in needles, melts at 157.5° , and is only slightly volatile in a current of steam; (2) 3-bromo-4-pyrone, $O \begin{array}{c} \text{CH:CB}r \\ \text{CH=CH} \end{array} CO$, which crystallises from light petroleum in prisms, softens at 109° , and melts at 114° ; (3) pentabromoacetone, and (4) an *oil* which on treatment with phenylhydrazine forms phenylhydrazine hydrobromide. When treated with ammonia in absolute alcoholic solution, 3:5-dibromo-4-pyrone yields only a small quantity of 3:5-dibromopyridone, $C_5H_3OBr_2N$, which crystallises in silvery leaflets and decomposes at about 300° .

The *perbromide*, formed by the action of an excess of bromine on 2:6-dimethyl-4-pyrone in presence of iodine, has approximately the formula $(C_7H_7O_2Br)_2 \cdot Br_2 \cdot HBr$ (compare Collie and Steele, *Trans.*, 1900, 77, 1114); it is obtained as a sulphur-yellow powder, does not colour carbon disulphide except in presence of water, liberates iodine from potassium iodide, and when boiled with water evolves bromine and yields bromo- and dibromo-dimethylpyrones, together with a polybromo-derivative of acetone.

3-Bromo-2:6-dimethyl-4-pyrone, $O \begin{array}{c} \text{CMe:CB}r \\ \text{CMe:CH} \end{array} CO$, crystallises from light petroleum in matted, white needles, melts at $75\text{—}76^\circ$, is easily soluble in water, ether, chloroform, or alcohol, reduces warm Fehling's solution, and, although less basic than 2:6-dimethyl- γ -pyrone, forms a *hydrobromide* which is partially decomposed by water and chloroform.

3:5-Dibromo-2:6-dimethyl-4-pyrone, $O \begin{array}{c} \text{CMe:CB}r \\ \text{CMe:CB}r \end{array} CO$, crystallises from boiling water or petroleum in slender needles, melts at $163\text{—}164^\circ$, sublimes partially, is not volatile in a current of steam, does not give a coloration with ferric chloride, and does not reduce

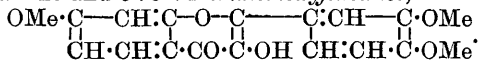
Fehling's solution; when boiled with aqueous barium hydroxide, it becomes slightly yellow, but does not form a yellow xantho-barium salt. When evaporated with aqueous ammonia or treated with ammonia in absolute alcoholic solution, it forms only a small amount of *dibromodimethylpyridone*, $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CMe} \cdot \text{CBr} \end{smallmatrix} \text{CO}$, which crystallises in glistening leaflets and melts and decomposes at 291° .

3-Bromo-2:6-dimethylpyridone, $\text{NH} \begin{smallmatrix} \text{CMe} \cdot \text{CBr} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{CO}$, formed in small quantity by the action of absolute alcoholic ammonia on 3-bromo-2:6-dimethyl-4-pyrone, decomposes at 292° . Bromo- and dibromo-2:6-dimethyl-4-pyrones do not yield the corresponding hydroxy- and dihydroxy-derivatives when treated with alkali hydroxides. With aqueous sodium hydroxide, the bromo-compound forms an oil which contains bromine and gives a brownish-red coloration with ferric chloride (compare Collie and Tickle, *Trans.*, 1902, **81**, 1004). When warmed with aqueous potassium hydroxide or calcium carbonate or with alcoholic sodium ethoxide, the dibromo-compound forms a small amount of a *substance*, $\text{C}_7\text{H}_7\text{O}_3\text{Br}$, which crystallises in white leaflets, melts at 106° , gives a bluish-red coloration with ferric chloride, and may have the constitution $\text{O} \begin{smallmatrix} \text{CMe} = \text{CBr} \\ \text{CMe} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{CO}$ or $\text{O} \begin{smallmatrix} \text{CHAc} \cdot \text{CO} \\ \text{CMe} = \text{CBr} \end{smallmatrix}$.

Ethyl dibromochelidonate, $\text{CO} \begin{smallmatrix} \text{CBr} \cdot \text{C}(\text{CO}_2\text{Et}) \\ \text{CBr} \cdot \text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} \text{O}$, is formed by the action of bromine on ethyl acetonedioxalate; it separates from ether in glistening crystals, melts at $126\text{--}127^\circ$ when heated with concentrated hydrochloric acid, and is decomposed with formation of oxalic acid. G. Y.

Synthesis of Fisetin. STANISLAUS VON KOSTANECKI and S. NITKOWSKI (*Ber.*, 1905, **38**, 3587—3589. Compare Kostanecki, Lampe, and Tambor, *Abstr.*, 1904, i, 441; Perkin, *Trans.*, 1904, **85**, 1459).—When boiled with acetic anhydride and sodium acetate, 2'-hydroxy-3:4:4'-trimethoxychalkone, obtained by condensation of paeonol with veratraldehyde, forms the *acetyl* derivative,

$\text{OAc} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, which crystallises from dilute alcohol in yellow needles and melts at 90° . 3:3':4'-Trimethoxyflavanone, melting at $120\text{--}121^\circ$, is obtained by boiling 2'-hydroxy-3:4:4'-trimethoxychalkone with alcoholic hydrochloric acid in a reflux apparatus. It forms the *isonitroso*-derivative, $\text{C}_6\text{H}_3(\text{OMe}) \cdot \text{O} \begin{smallmatrix} \text{CO} - \text{C}(\text{N} \cdot \text{OH}) \end{smallmatrix} \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$, which crystallises from benzene in almost white needles, melts and decomposes at 183° , and when boiled with glacial acetic acid and 10 per cent. sulphuric acid is hydrolysed to hydroxylamine and 3:3':4'-trimethoxyflavanol,

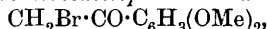


This crystallises from alcohol in yellow needles, melts at 186° , dissolves in alcohol to form a solution with green fluorescence, and forms a sparingly soluble *sodium* derivative and an *acetyl* derivative,

$C_{15}H_{10}O_2(OMe)_3 \cdot OAc$, crystallising in white needles and melting at 170° .

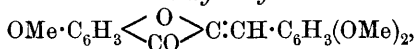
When boiled with concentrated hydriodic acid, 3:3':4'-trimethoxyflavanol and its acetyl derivative are converted into fisetin (3:3':4'-trihydroxyflavanol).
G. Y.

3-Methoxycoumaranone. A. BLOM and JOSEF TAMBOR (*Ber.*, 1905, 38, 3589—3592. Compare Feuerstein and Kostanecki, *Abstr.*, 1899, i, 538).—The action of bromoacetyl bromide and aluminium chloride on *m*-dimethoxybenzene in carbon disulphide solution leads to the formation of *α*-bromoresacetophenone dimethyl ether,



which crystallises from dilute alcohol in small, colourless needles, melts at 102° , and when boiled with potassium acetate in absolute alcoholic solution in a reflux apparatus yields 3-methoxycoumaranone,

$OMe \cdot C_6H_3 < \begin{smallmatrix} O \\ CO \end{smallmatrix} > CH_2$. This crystallises from alcohol in yellow needles, melts at 125° , dissolves in concentrated sulphuric acid to form a solution which gradually assumes a green fluorescence, and condenses with veratraldehyde in aqueous-alcoholic sodium hydroxide solution to form 3:3':4'-trimethoxybenzylidenecoumaranone,



which crystallises from alcohol in slender, glistening, yellow needles and melts at 189° (compare Emilewicz and Kostanecki, *Abstr.*, 1899, i, 368; Kostanecki and Rózycki, *ibid.*, 911). It is formed also by the action of hot alcoholic potassium hydroxide on 2'-acetoxy-3:4:4'-trimethoxychalkone dibromide,



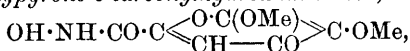
which is obtained by treating 2'-acetoxy-3:4:4'-trimethoxychalkone (Kostanecki and Nitkowski, preceding abstract) with bromine in carbon disulphide solution, crystallises from a mixture of chloroform and light petroleum in rosettes of needles, and melts and decomposes at 122° .

G. Y.

Action of Hydroxylamine and α -Benzylhydroxylamine on Ethyl Hydroxytrimethylcomenate. E. AZZARELLO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 162—167).—Meyer (*Abstr.*, 1884, 993) and Odernheimer (*Abstr.*, 1884, 1302) have shown that comenic acid does not react with hydroxylamine, whilst ethylcomenic acid and ethyl diethylcomenate yield with it hydroxypyridine derivatives. Similarly, hydroxycomenic acid, being non-etherified, only gives a salt with hydroxylamine, or, when heated with excess of the latter, resinifies; the ester of its trimethyl derivative gives, however, a hydroxamic acid with hydroxylamine, but with α -benzylhydroxylamine reaction only takes place with difficulty, and yields probably the benzyl derivative of the corresponding oxy-pyridone compound.

Hydroxylamine hydroxycomenate separates from water in pale yellow crystals carbonising at about 200° , reduces Fehling's solution in the cold, and, when heated in alcoholic solution with piperonal, yields piperonaloxime.

2:3-Dimethoxypyrrone-6-carbonylhydroxamic acid,



prepared by the interaction of ethyl hydroxytrimethylcomenate and hydroxylamine in alcoholic solution, crystallises from ethyl acetate in white needles, melting and decomposing at 178—179°, and is soluble in water, methyl or ethyl alcohol, or acetone. It has an acid reaction, reduces Fehling's solution and ammoniacal silver nitrate solution on heating, and gives a cherry-red coloration with ferric chloride and, with copper acetate, a green precipitate dissolving in excess of the acetate solution. Its *barium* salt, $(\text{C}_8\text{H}_8\text{O}_6\text{N})_2\text{Ba}\cdot 2\text{H}_2\text{O}$, separates from water in small, white needles which undergo change at 110—120°. When heated with 20 per cent. sulphuric acid, the acid undergoes decomposition into hydroxylamine and dimethoxypyrronecarboxylic acid.

T. H. P.

Basicity of Pyranic Oxygen. Double Salts of Halogen Derivatives of Dinaphthapyryl and of the Metals. ROBERT FOSSE and L. LESAGE (*Compt. rend.*, 1905, 141, 625—626).—In addition to the double halogen salts of dinaphthapyryl and certain metals already described (compare this vol., i, 541), similar compounds containing the metals platinum, lead, iron, zinc, tin, bismuth, arsenic, or antimony have also been prepared; the formulæ of these new salts are given below, the dinaphthapyryl group $\left[\cdot\text{CH}\begin{array}{c} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{array}\text{O}\right]$ being represented by R: PtBr₄, 2RBr, red powder. PtCl₂, RCl, violet-red crystals. FeCl₃, RCl, orange powder. ZnCl₂, 2RCl, red crystals, yellow in reflected light. 3ZnBr₂, 4RBr, red crystals, green in reflected light. SnBr₄, 2RBr, red crystals, yellow in reflected light. BiBr₃, 3RBr, bright red powder. AsBr₃, RBr, red crystals. SbBr₃, RBr, red crystals.

M. A. W.

β-Coniceine. KARL LÖFFLER (*Ber.*, 1905, 38, 3326—3329. Compare Hofmann, Abstr., 1885, 401).—When conhydrine is heated with phosphoric oxide at 180—190° for 20 minutes, according to Wertheim (*Annalen*, 1856, 100, 75) the products are β-coniceine and a small amount of a liquid, unsaturated, secondary base, but no α-coniceine. β-Coniceine has a sp. gr. 0.8519 at 50°/50° and $[\alpha]_D - 52.99^\circ$ at 42°. The *hydrochloride* crystallises in glistening needles and melts at 177—181°. The *aurichloride* melts at 122.5°, the *picrate* and *cadmioidide* are oily.

Larger quantities of the oily base are obtained when the heating is carried out for a longer time and at a higher temperature, for example, for one hour at 220°.

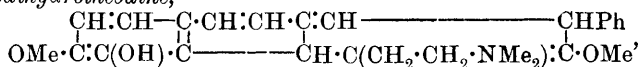
J. J. S.

Hydroxysparteine. FELIX B. AHRENS (*Ber.*, 1905, 38, 3268).—Hydroxysparteine, C₁₅H₂₄ON₂, is obtained in the theoretical yield by adding an alkaline solution of potassium ferricyanide to sparteine until the colour of the oxidising agent remains unchanged; the product is extracted with ether or chloroform.

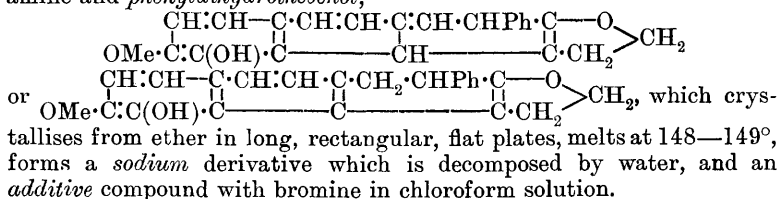
G. Y.

Action of Bromine on Strychnine. HEINRICH BECKURTS (*Arch. Pharm.*, 1905, **243**, 493—495. Compare Abstr., 1890, 1329).—When a dilute solution of strychnine hydrobromide is mixed with excess of bromine, *bromostrychnine tribromide*, $C_{21}H_{21}O_2N_2Br_3$, is obtained as a yellow, crystalline powder, which carbonises without melting when heated, and is sparingly soluble in cold alcohol, insoluble in water. When heated at 105° or digested with cold alcohol, it is converted into a dibromide. Boiling with alcohol or treatment in the cold with alcoholic potassium hydroxide, hydrogen sulphide, or zinc and sulphuric acid converts it into bromostrychnine and a bromide or hydrobromic acid. C. F. B.

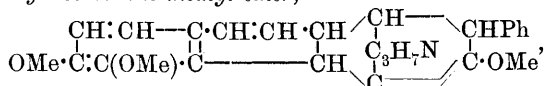
Thebaine. MARTIN FREUND (*Ber.*, 1905, **38**, 3234—3256).—Thebaine interacts with magnesium phenyl bromide in ethereal solution to form *phenyldihydrothebaine hydriodide*, $C_{25}H_{27}O_3N, HI$, which crystallises from water and melts at 230 — 232° , or from alcohol in prisms containing C_2H_6O and melting at 182 — 184° . The free *base* crystallises from a small quantity of alcohol in prisms and melts at 60 — 65° ; the *sodium* derivative forms matted needles; the *hydrochloride*, $C_{25}H_{27}O_3N, HCl, C_2H_6O$, crystallises from alcohol in prisms and melts and decomposes at 145 — 147° ; the *hydrobromide* crystallises in plates and melts and decomposes at 190 — 195° ; the *methiodide*, $C_{26}H_{30}O_3NI$, crystallises from 50 per cent. alcohol in prisms and melts at 230 — 231° . When boiled with 30 per cent. potassium hydroxide or with sodium ethoxide solution, the methiodide yields *dephenyl-N-methyldihydrothebaine*,



which sinters at 55° , melts at 90° , is readily soluble in most organic solvents, and forms the *methiodide*, $C_{27}H_{32}O_3NI$. This crystallises from dilute alcohol in matted needles, sinters at 145 — 155° , and when boiled with concentrated aqueous potassium hydroxide or absolute alcoholic sodium ethoxide is decomposed with formation of trimethylamine and *phenyldihydrothebenol*,

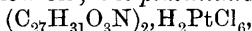


Phenyldihydrothebaine methyl ether,

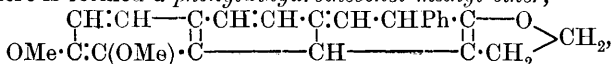


is formed by digesting phenyldihydrothebaine with sodium ethoxide and methyl *p*-toluenesulphonate in alcoholic solution; it separates from aqueous alcohol as a flocculent precipitate which becomes crystalline, sinters at 60° , and is melted at about 70° . It combines with methyl

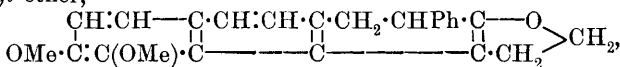
iodide to form the *methiodide*, $C_{27}H_{32}O_3NI$, which crystallises in long plates, melts at $209-210^\circ$, and when boiled with alcoholic sodium ethoxide yields *dephenyl-N-methyldihydrothebaine methyl ether*, which is obtained as a viscid, yellow oil; the *platinichloride*,



is amorphous and melts at $125-135^\circ$. When the base is treated with methyl iodide and the product boiled with sodium ethoxide solution, there is formed *α -phenyldihydrothebenol methyl ether*,

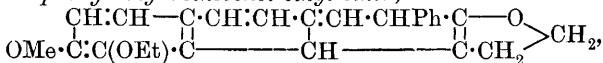


which is formed also by the action of methyl iodide and sodium ethoxide on phenyldihydrothebenol; it crystallises from alcohol in hexagonal prisms, melts at $114-115^\circ$, and is optically inactive. When heated over its melting point, the α -methyl ether changes into the β -methyl ether,



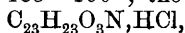
which is formed also when the α -isomeride is boiled with amyl alcohol or heated with acetic anhydride and sodium acetate in a sealed tube at 100° ; it crystallises in rhombic plates, melts at $123-124^\circ$, and is optically inactive. Both ethers form unstable *additive* compounds with sodium ethoxide in alcoholic solution, and yield phenyldihydrothebenol when dried over soda-lime and treated with water.

Phenyldihydrothebaine ethyl ether methiodide, $C_{28}H_{34}O_3NI$, is formed when phenyldihydrothebaine is treated with sodium ethoxide and ethyl iodide in alcoholic solution on the water-bath and the oily product boiled with methyl iodide and a small quantity of alcohol in a reflux apparatus; it crystallises from dilute alcohol in long prisms, melts at $209-210^\circ$, and when boiled with concentrated sodium ethoxide solution yields *dephenyl-N-methyldihydrothebaine ethyl ether*, which is a viscid oil with blue fluorescence, is soluble in acids, and on digestion with methyl iodide and a small quantity of alcohol yields the *methiodide*, $C_{29}H_{36}O_3NI$. This crystallises in white plates, melts at $247-248^\circ$, and when digested with sodium ethoxide solution yields an amine and *phenyldihydrothebenol ethyl ether*,



which is formed also by the action of sodium ethoxide and ethyl iodide on phenyldihydrothebenol, crystallises in long, flat prisms, and melts at $97-98^\circ$. When boiled with acetic anhydride and sodium acetate, phenyldihydrothebaine forms an *acetyl* derivative, $C_{27}H_{29}O_4N$, which forms a granular mass, sinters at $65-70^\circ$, melts at 92° , and forms a *methiodide*, $C_{28}H_{32}O_4NI$; this crystallises in short, stout prisms and melts at $202-203^\circ$.

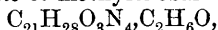
When boiled with hydriodic acid of sp. gr. 1.7, phenyldihydrothebaine hydriodide yields methyl iodide and the *hydriodide* of *nor*-phenyldihydrothebaine, which crystallises from water in matted needles and melts at about $185-190^\circ$; the *hydrochloride*,



ing at $200-201^{\circ}$ (corr.), or from methyl alcohol in yellow needles containing CH_4O ; the *semicarbazone*, $\text{C}_{19}\text{H}_{24}\text{O}_3\text{N}_4$, crystallises in colourless needles and melts at 227° (corr.); the *phenylhydrazone* is not crystalline; the *methiodide*, $\text{C}_{19}\text{H}_{24}\text{O}_3\text{NI}$, crystallises in colourless prisms and melts at $255-256^{\circ}$ (corr.). The *acetyl* derivative, $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}$, crystallises in small prisms and melts at $100-101^{\circ}$ (corr.); the *methiodide* of the acetyl derivative, $\text{C}_{21}\text{H}_{26}\text{O}_4\text{NI}$, crystallises from the concentrated alcoholic solution in colourless prisms and melts at $223-225^{\circ}$ (corr.); the *semicarbazone* of acetylthebainone crystallises from ethyl acetate in colourless needles and melts at 249° (corr.); the *phenylhydrazone*, $\text{C}_{26}\text{H}_{29}\text{O}_3\text{N}_3$, forms yellow prisms and melts at $225-226^{\circ}$ (corr.).

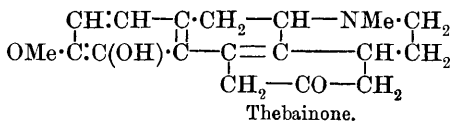
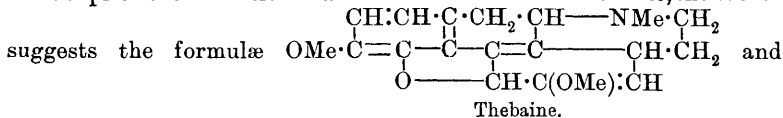
Thebainol, $\text{C}_{18}\text{H}_{23}\text{O}_3\text{N}$, is obtained when the ketone is reduced with sodium amalgam in dilute sodium hydroxide solution; it crystallises from its concentrated methyl-alcoholic solution in colourless, prismatic needles, and melts at $54-55^{\circ}$ or, after fusion in a vacuum and re-solidification, at $76-78^{\circ}$ (corr.).

Thebainone methyl ether (methylthebainone), $\text{C}_{19}\text{H}_{23}\text{O}_3\text{N}$, can be prepared by treating the ketone with diazomethane in ethereal alcoholic solution; it crystallises from methyl alcohol in slightly yellow, prismatic plates and melts at 156° (corr.). The action of methyl iodide on the ketone or its methyl ether in sodium methoxide solution leads to the formation of *methylthebainone methiodide*, $\text{C}_{20}\text{H}_{26}\text{O}_3\text{NI}$, which crystallises in hexagonal leaflets and melts at 256° (corr.). When warmed with 30 per cent. aqueous sodium hydroxide, this yields *methylthebainonemethine*, $\text{C}_{20}\text{H}_{25}\text{O}_3\text{N}$, which crystallises from a mixture of ether and light petroleum in slender, yellow needles, and, after being dried at 90° in a vacuum, melts at $65-66^{\circ}$ (corr.). The *methiodide*, $\text{C}_{21}\text{H}_{28}\text{O}_3\text{NI}\cdot\text{C}_2\text{H}_6\text{O}$, crystallises from its ethereal-alcoholic solution in glistening, yellow needles, loses $\text{C}_2\text{H}_6\text{O}$ at 100° , and melts at $171-172^{\circ}$ (corr.). The *semicarbazone* of methylthebainonemethine,



crystallises in long, yellow, hexagonal leaflets, sinters at 85° , and melts at $107-108^{\circ}$ (corr.), or, after losing $\text{C}_2\text{H}_6\text{O}$ at 90° in a vacuum, at $126-127^{\circ}$ (corr.). The *hydrochloride* of methylthebainonemethine oxime, $\text{C}_{20}\text{H}_{26}\text{O}_3\text{N}_2\cdot\text{HCl}$, formed by the action of hydroxylamine hydrochloride and sodium acetate on the ketone in acetic acid solution, crystallises in yellow prisms, melts at $271-272^{\circ}$ (corr.), and on treatment with aqueous potassium carbonate yields an amorphous *base* which is easily soluble in the usual organic solvents.

To explain the formation of a ketone on reduction of thebaine, the author



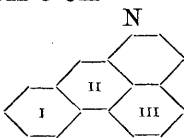
Thebainone from Codeinone. LUDWIG KNORR (*Ber.*, 1905, **38**, 3171. Compare preceding abstract).—Thebainone is formed by reduction of codeinone with stannous chloride and hydrochloric acid in a sealed tube at 100°; it is a dihydrocodeinone isomeric with codeine. G. Y.

Decomposition Products of Thebainone. LUDWIG KNORR and ROBERT PSCHORR (*Ber.*, 1905, **38**, 3172—3181. Compare preceding abstracts).—Thebainone, $\text{OMe} \cdot \text{C}_{14}\text{H}_{10}\text{O}(\text{OH}) < \begin{smallmatrix} \text{C}_2\text{H}_4 \\ | \\ \text{NMe} \end{smallmatrix}$, stands between codeinone, $\text{OMe} \cdot \text{C}_{14}\text{H}_9\text{O}_2 < \begin{smallmatrix} \text{C}_2\text{H}_4 \\ | \\ \text{NMe} \end{smallmatrix}$, on the one hand, and morphothebaine, $\text{OMe} \cdot \text{C}_{14}\text{H}_7(\text{OH})_2 < \begin{smallmatrix} \text{C}_2\text{H}_4 \\ | \\ \text{NMe} \end{smallmatrix}$, and thebinine, $\text{OMe} \cdot \text{C}_{14}\text{H}_6(\text{OH})_2 \cdot \text{C}_2\text{H}_4 \cdot \text{NHMe}$, on the other. It resembles the last two in the presence of a hydroxyl group in the place of the indifferent oxygen atom of the opium alkaloids, but differs from them in its degree of reduction.

A table is given showing the most important decomposition products of the opium alkaloids and their derivatives, and the following conclusions are drawn as to the constitutions of morphine, codeine, and thebaine: (1) they are derivatives of 3:6-dihydroxyphenanthrylene

oxide, $\text{OH} \cdot \text{C} \begin{array}{c} \text{O} \\ \text{---} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{O} \\ \text{---} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{O} \\ \text{---} \end{array} \text{C} \cdot \text{OH}$; in codeine one, and in thebaine two of the hydroxyl groups are methylated. (2) The group $\cdot \text{C}_2\text{H}_4 \cdot \text{NMe} \cdot$ is attached to the phenanthrene nucleus as a side ring; it remains to be determined whether as the group $\cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe} \cdot$ or as $\cdot \text{CHMe} \cdot \text{NMe} \cdot$, but the constitution of papaverine,

$$\begin{array}{c} \text{OMe} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{C} [\text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2] \cdot \text{N} \\ | \quad | \quad | \\ \text{OMe} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CH} \end{array} \text{---} \text{CH},$$

points to the structure  for the nucleus of the mor-

phine alkaloids. (3) So far as is known at present, morphine is 3:6-dihydroxy-8:9(?)-ethylenemethylaminohexahydrophenanthrylene 4:5-oxide, the rings II and III of the phenanthrene nucleus being reduced, whilst I remains as a benzene ring; codeine is 6-hydroxy-3-methoxy-8:9(?)-ethylenemethylaminohexahydrophenanthrylene 4:5-oxide; and thebaine, 3:6-dimethoxy-8:9(?)-ethylenemethylaminophenanthrylene 4:5-oxide.

When heated with acetic anhydride at 170—180° for 48 hours, methylthebainonemethine yields dimethylmorphol melting at 43—44°, and dimethylhydroxyethylamine. This shows that the formation of alcohol bases is not dependent on a linking of the group $\cdot \text{C}_2\text{H}_4 \cdot \text{NMe} \cdot$, by means of an oxygen atom, to the phenanthrene nucleus, but may take place by solution of a carbon union.

Methylthebainonemethine is decomposed by sodium ethoxide in

alcoholic solution at 150—160° with formation of a resinous phenanthrene derivative and dimethylethylamine, which forms an aurichloride melting at 220° and a *platinichloride* decomposing at about 240° (compare Skraup and Wiegmann, Abstr., 1889, 1018).

The *base* obtained on treating methylthebainonemethine methiodide with silver oxide decomposes at 150—160°, with formation of a phenanthrene derivative and trimethylamine. G. Y.

Complex Molybdenum Thiocyanates. JULIUS SAND and O. BURGER (*Ber.*, 1905, 38, 3384—3389).—When a solution of ammonium molybdate and ammonium thiocyanate is reduced electrolytically and the resulting liquid extracted with ether, all the red colouring substances pass into the latter; on adding pyridine, *molybdenumdipyridinetetrathiocyanate*, $\text{Mo}[(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_4]$, is obtained in the form of dark brownish-red, feathery aggregates of crystals. When the foregoing red solution is extracted with amyl alcohol and a large excess of pyridine is added, the *hexathiocyanate*,

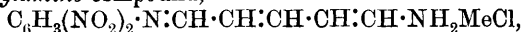
$\text{Mo}(\text{C}_5\text{H}_5\text{N}, \text{HCNS})_2(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_4$, is obtained; it crystallises in well-formed, bright yellow plates and melts at 115°.

Molybdenumtetraquinolinetetrathiocyanate, $\text{Mo}(\text{C}_9\text{H}_7\text{N})_4(\text{CNS})_4$, obtained by adding quinoline to the ethereal extract of the foregoing reduced solution, forms beautiful, brownish-violet crystals.

Molybdenumhexapyridinedecachloride, $\text{Mo}(\text{C}_5\text{H}_5\text{N}, \text{HCl})_6\text{Cl}_4$, is obtained by passing hydrogen chloride into a solution of molybdenumdipyridinetetrathiocyanate in acetone; it forms yellowish-green, hygroscopic crystals. The probable relationship of the foregoing substances is discussed. W. A. D.

Dinitrophenylpyridinium Chloride and its Transformation Products. IV. The Action of Aliphatic Amines on Dinitrophenylpyridinium Chloride. THEODOR ZINCKE and W. WÜRCKER (*Annalen*, 1905, 341, 365—379. Compare Abstr., 1904, i, 921).—The aliphatic amines differ from the aromatic amines in their behaviour towards dinitrophenylpyridinium chloride. Amorphous substances which yield red hydrochlorides are at first formed, dinitroaniline not being eliminated. Prolonged treatment, however, causes the formation of dinitroaniline and quaternary pyridinium salts. The red salts are related to the substances produced by the action of alkalis and phenylhydrazine on the pyridinium compound. These red salts are represented by the formula $[\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{C}_5\text{NH}_5] \cdot \text{NHAlk}, \text{HCl}$; they are decomposed by aniline with the formation of the dianilide (compare Abstr., 1904, i, 923). When heated with hydrochloric acid, dinitroaniline is formed, and a pyridinium salt, $\text{C}_5\text{NH}_5\text{AlkCl}$, in the case of the compounds of primary amines. The products obtained from secondary amines are decomposed to a much greater extent by hydrochloric acid. Primary aliphatic amines do not yield compounds corresponding with the dianilides. Secondary amines, on the other hand, give such compounds, which, however, are unstable.

The *methylamine* compound,

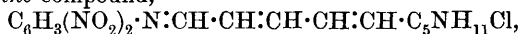


prepared by addition of 10 per cent. aqueous methylamine to a solution of dinitrophenylpyridinium chloride, followed by addition of hydrochloric acid, crystallises in intensely red leaflets, melting and decomposing at 120—121°. The *platinichloride* is a pale red, crystalline powder, melting and decomposing at 150°. The free base is a dark brown precipitate. The *ethylamine* compound, $C_{13}H_{15}O_4N_4Cl$, forms red, metallic needles melting and decomposing at 105°; the *ethylenediamine* compound melts and decomposes at 131—133°. Methylpyridinium chloride, C_5NH_5MeCl , prepared by heating the methylamine derivative with hydrochloric acid, or directly from dinitrophenylpyridinium chloride, forms a *mercurichloride*, which crystallises in needles melting and decomposing at 189—191°. The *platinichloride*, $(C_5NH_5Me)_2PtCl_6$, crystallises in orange-yellow leaflets melting at 203—204°.

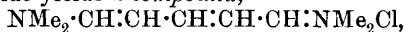
The *dimethylamine* compound,



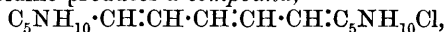
prepared in the same manner as the methylamine compound, crystallises in pale yellow needles melting and decomposing at 116—117°; the *platinichloride* is a brick-red, crystalline powder. The *diethylamine* compound crystallises in red needles melting and decomposing at 170°. The *piperidine* compound,



crystallises in red needles melting and decomposing at 126—128°; the *platinichloride* is a dark red, crystalline powder melting and decomposing at 179—180°. With excess of dimethylamine, the dinitrophenylpyridinium chloride yields a *compound*,



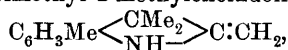
the *platinichloride* of which crystallises in orange-red plates melting and decomposing at 153—154°. The *mercurichloride* is a pale yellow precipitate and the *stannochloride* a pale brown precipitate, while the *double salt* with cadmium sulphate crystallises in yellow needles. Excess of piperidine produces a *compound*,



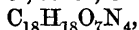
which forms a *mercurichloride*, $C_{15}H_{25}N_2Cl, HgCl_2$, as a yellow, crystalline, unstable precipitate melting and decomposing at 183°.

K. J. P. O.

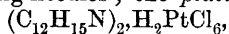
A New Methyleneindoline Base. ARTUR KONSCHEGG (*Monatsh.*, 1905, 26, 931—937. Compare Brunner, *Abstr.*, 1896, i, 169, 253; 1900, i, 360).—The *p-tolylhydrazone* of methyl isopropyl ketone forms a slightly yellow oil, which boils at 164° under 30 mm. pressure and rapidly becomes red on exposure to air. When treated with an alcoholic solution of stannous chloride and hydrochloric acid after eight days at the ordinary temperature, warmed on the water-bath, and finally precipitated with ether and hydrogen chloride, the hydrazone yields the *stannochloride* of 3 : 3 : 5-trimethyl-2-methyleneindoline. The *base*,



forms a red, aromatic oil, which boils at 170° under 30 mm. pressure and is readily soluble in alcohol, ether, or acids. The *picrate*,



crystallises in slender, yellow needles and melts at 195° ; the *mercurichloride* crystallises in long needles; the *platinichloride*,



forms a bronze-red powder; the *ferrichloride* is obtained as an oil. With potassium nitrite and dilute sulphuric acid, the base forms an oily *nitrosoamine*, which gives Liebermann's reaction. The *acetyl* derivative crystallises from light petroleum and is hydrolysed by boiling 20 per cent. aqueous sodium hydroxide; the aqueous solution yields a residue which gives the cacodyl reaction. The *benzoyl* derivative crystallises from dilute alcohol in thread-like needles.

Plancher's supposed 2 : 3 : 3-trimethylindolenine (Abstr., 1898, i, 536) is 3 : 3-dimethyl-2-methyleneindoline. G. Y.

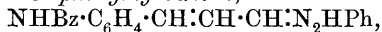
Action of Bromine on Chloroindole and of Sulphuryl Chloride on Scatole. GIROLAMO MAZZARA and ALESSANDRO BORGIO (*Gazzetta*, 1905, 35, ii, 326—333. Compare following abstract).—The constitution of the compound formed by the action of sulphuryl chloride (1 mol.) on indole (1 mol.) is proved by treating it with bromine (1 mol.), which converts it into 2-chloro-3-bromo-indole, $\text{C}_8\text{NH}_5\text{ClBr}$; this compound crystallises from light petroleum in faintly yellow, shining scales turning brown at 85° and softening and decomposing at 92° ; it dissolves in dilute potassium hydroxide solution and in concentrated sulphuric acid, to which it imparts an intensely green colour. When heated, in methyl-alcoholic solution, with alcoholic potassium hydroxide and methyl iodide, it yields 2-chloro-3-bromo-1-methylindole, $\text{C}_8\text{NH}_4\text{MeClBr}$, which crystallises from aqueous alcohol in slender, silky needles melting at 59° , and dissolves in the cold in concentrated sulphuric acid, giving it a yellow, and later a green coloration.

2-Chloro-3-methylindole, $\text{C}_8\text{NH}_5\text{MeCl}$, prepared by the action of sulphuryl chloride (1 mol.) on scatole (1 mol.), crystallises from light petroleum in small, white leaflets readily turning yellow, even in presence of the solution, and melts at 112° ; it has an intense, rather pleasing odour and is soluble to a slight extent in water and more readily in concentrated sulphuric acid, to which it imparts a pale yellow coloration. T. H. P.

Action of Sulphuryl Chloride on Indole. GIROLAMO MAZZARA and ALESSANDRO BORGIO (*Gazzetta*, 1905, 35, ii, 320—326. Compare this vol., i, 827).—Sulphuryl chloride acts on indole with apparent formation of monochloroindole, which could not be purified, as it readily changes into oxindole. The latter separates from light petroleum in long needles or prisms melting at 125° , which is some 5° higher than the melting points given by Baeyer and Knop (*Annalen*, 1866, 140, 29) and by König and Reissert (Abstr., 1899, i, 457). Oxindole can only be formed by the action of water on 2-chloroindole, but all attempts to separate the latter from the other products of the action of sulphuryl chloride on indole have been unsuccessful. T. H. P.

Introduction of Benzoyl Groups into Tertiary Cyclic Bases.
II. ARNOLD REISSERT (*Ber.*, 1905, 38, 3415—3435. Compare this vol., i, 472).—The substance formed by the action of benzoyl chloride

and sodium hydroxide on quinoline, and supposed to be 2-hydroxy-1-benzoyl-1 : 2-dihydroquinoline (*loc. cit.*), is really *o*-benzoylaminocinnamaldehyde, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CHO}$. With hydroxylamine, it gives the *oxime*, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{N} \cdot \text{OH}$, which crystallises from methyl or ethyl alcohol in small needles and melts and decomposes at 170—171°. The *phenylhydrazone*,



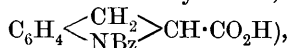
crystallises from glacial acetic acid in small, yellow needles and melts at 183—184°.

o-Benzoylaminocinnamylideneaniline,



prepared by the action of aniline on the aldehyde, crystallises from alcohol in pale yellow needles and melts at 144—145°; on prolonged boiling with alcohol, it is decomposed, giving benzanilide and quinoline. *o*-Benzoylaminocinnamaldehyde does not interact with methylaniline.

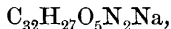
o-Benzoylaminocinnamic acid, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$, prepared by oxidising the aldehyde with silver oxide in presence of sodium hydroxide in alcohol, crystallises from alcohol in small, flat needles and melts and decomposes at 262°; it is identical with the substance prepared by benzoylating *o*-aminocinnamic acid, and on hydrolysis with hydrochloric acid at 160—180° gives benzoic acid and carbostyryl. The substance formerly described as *o*-benzoylaminocinnamic acid (Walter, *Abstr.*, 1892, 881) and prepared by the oxidation of *N*-benzoyltetrahydroquinoline, has apparently another structure (perhaps 1-benzoylhydroindole-2-carboxylic acid,



as on hydrolysis it gives benzoic acid, carbon dioxide, indole, and hydrogen.

o-Benzoylamino- β -phenylpropionic acid, $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, prepared by reducing *o*-benzoylaminocinnamic acid with sodium amalgam and benzoylating the product (*o*-amino- β -phenylpropionic acid) in alkaline solution, forms small, soft crystals and melts indefinitely at 153—170°.

On warming *o*-benzoylaminocinnamaldehyde with alcoholic potassium hydroxide, an *acid* is formed according to the equation $2\text{C}_{16}\text{H}_{13}\text{O}_2\text{N} + \text{H}_2\text{O} = \text{C}_{32}\text{H}_{28}\text{O}_5\text{N}_2$; on precipitating with hydrochloric acid, the *lactone*, $\text{C}_{32}\text{H}_{26}\text{O}_4\text{N}_2$, is obtained, which crystallises from acetone in small, hard, very white crystals and melts at 268—269°. The *sodium* salt,

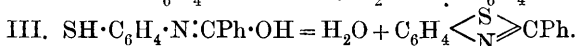
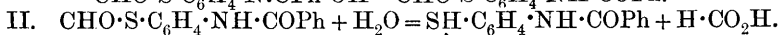
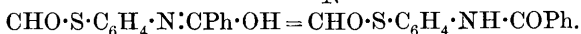


and *silver* salt, $\text{C}_{32}\text{H}_{27}\text{O}_5\text{N}_2\text{Ag}$, of the acid were prepared. On heating the lactone with concentrated hydrochloric acid at 160—170°, a *base*, $\text{C}_{18}\text{H}_{16}\text{ON}_2$, is formed which gives, on benzoylation, a *benzoyl* derivative, $\text{C}_{25}\text{H}_{20}\text{O}_2\text{N}_2$; this crystallises from acetic acid in small prisms, sinters at 158°, and decomposes at 174°. The probable nature of the foregoing substances is discussed.

When *isoquinoline* is caused to interact with benzoyl chloride and potassium cyanide at the ordinary temperature, 1-cyano-2-benzoyl-1 : 2-dihydroisoquinoline, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH} = \text{CH} \\ \text{C}(\text{NBz}) \cdot \text{CH} \cdot \text{CN} \end{smallmatrix}$, is formed; it crystallises from alcohol in small, colourless prisms, melts at 125—126°, and is

decomposed by concentrated hydrochloric acid at the ordinary temperature, giving a mixture of *isoquinaldic acid* (*isoquinoline-1-carboxylic acid*) and its *amide*. The former separates from benzene in compact, yellow crystals, melts and decomposes at 161° ; the latter crystallises from benzene in small needles and melts at $168-169^{\circ}$. Two other *substances*, the one melting at 151° , the other, $C_{24}H_{23}ON_3$, at $123-124^{\circ}$, are produced in small quantity at the same time.

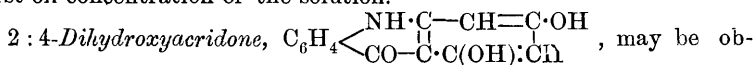
When benzthiazole in aqueous suspension is acted on by benzoyl chloride and sodium hydroxide, a mixture of 1-phenylbenzthiazole and *dibenzoyl-o-aminothiophenol*, $NHBz \cdot C_6H_4 \cdot SBz$, is obtained; the latter crystallises from alcohol in thin needles, melts at $154-155^{\circ}$, and when boiled with 10 per cent. sodium hydroxide gives *oo'*-diaminodiphenyl disulphide. It is probable that the foregoing products are formed in accord with the equations: I. $C_6H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ N \end{smallmatrix} CH + Ph \cdot CO \cdot OH =$



Pyridine and acridine could not be made to interact with benzoyl chloride in presence of either sodium hydroxide or potassium cyanide.

W. A. D.

Dihydroxyacridone and its Derivatives. W. BACZYŃSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1905, **38**, 3009—3017. Compare Niementowski, *Abstr.*, 1896, i, 261).—2:4-Dihydroxyacridone and its anilide are formed along with hydroxyquinacridone when anthranilic acid and phloroglucinol are heated together at $170-190^{\circ}$ for half an hour. On extraction of the product with boiling acetone, 2:4-dihydroxyacridone and its anilide dissolve, the former crystallising out first on concentration of the solution.



tained from the reaction product also by extraction with boiling aqueous sodium hydroxide, and is then purified by means of its sodium derivative; it crystallises in canary-yellow, nodular aggregates of needles, melts at 370° , is easily soluble in acetone, less so in methyl or ethyl alcohol, ethyl acetate, or glacial acetic acid, and only sparingly so in boiling water, has marked acid properties, and is easily soluble in aqueous ammonia or alkali hydroxides, but insoluble in dilute acids. The *sodium* derivative, $C_{13}H_8O_3NNa \cdot 5H_2O$, crystallises in slender, glistening, yellow needles, dyes silk yellow, and is decomposed by carbon dioxide in aqueous solution. The *acetyl* derivative, $C_{13}H_8O_3NAc$, formed by boiling 2:4-dihydroxyacridone with acetic anhydride and sodium acetate, separates from ethyl acetate in stout yellow crystals, softens at 195° , melts at 200° , is more soluble than the dihydroxyacridone in organic solvents, dissolves readily in aqueous alkali hydroxides, sparingly in ammonia, and is insoluble in dilute acids; it is very stable towards hydrolysing agents. The *benzoyl* derivative, $C_{20}H_{13}O_4N$, formed by the Schotten-Baumann method, crystallises in glistening, greenish-yellow, thin leaflets and melts at

295—297°. The action of methyl iodide on the sodium derivative of 2:4-dihydroxyacridone in methyl-alcoholic solution at 150° leads to the formation of two monomethyl ethers. The α -methyl ether, $C_{14}H_{11}O_3N$, crystallises in spherical, chocolate-coloured aggregates, sinters at 190°, melts at 203°, and is moderately soluble in hot alcohol, acetone, aqueous ammonia, or alkali hydroxides. The β -methyl ether crystallises in glistening, yellow, thin leaflets, sinters at 235°, melts and decomposes at 252°, and is more soluble than the α -isomeride in organic solvents.

The action of a large excess of methyl sulphate on 2:4-dihydroxyacridone leads to the formation of the β -monomethyl ether and 2:4-dimethoxyacridone, $C_{15}H_{13}O_3N$, which crystallises in green, nodular aggregates, becomes a dull green at 225°, and melts and decomposes at 286—287°; it is in general less soluble than the β -, but more so than the α -monomethyl ether.

α -Nitro-2:4-dihydroxyacridone, $C_{13}H_8O_5N_2$, is formed by the action of boiling dilute nitric acid on 2:4-dihydroxyacridone; it separates from organic solvents in yellow crystals, melts and decomposes at 257°, and is soluble in aqueous alkali hydroxides, ammonia, or mineral acids.

β -Nitro-2:4-dihydroxyacridone, formed by the action of nitric acid of sp. gr. 1.55 at 0—3° on 2:4-dihydroxyacridone, separates from acetone in dark brown crystals, becomes green at 180°, melts and decomposes at 268°, and is soluble in aqueous alkali hydroxides or ammonia, but only sparingly so in dilute acids.

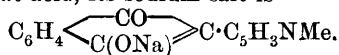
The *anilide*, $C_{19}H_{14}O_2N_2$, crystallises in metallic, yellow, microscopic leaflets, melts at 269—270°, is easily soluble in methyl or ethyl alcohol, acetic acid or acetone, and yields aniline and 2:4-dihydroxyacridone when heated with concentrated hydrochloric acid at 200°.

An isomeric *anilide*, melting at 138—140°, is formed when dihydroxyacridone is heated with aniline in a sealed tube at 200°. G. Y.

α' -Methyl- α -pyrophthalone. ALEXANDER EIBNER (*Ber.*, 1905, 38, 3353—3354. Compare Scholze, this vol., i, 825).—Scholze's 2-methyl-6-pyrophthalone is represented as having the constitution

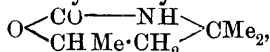


and as it is a *pseudo*-acid, its sodium salt is



J. J. S.

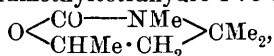
Derivatives of Diacetonalkamines. IV. MORITZ KOHN (*Monatsh.*, 1905, 26, 939—949. Compare Abstr., 1904, i, 378, 932, 933).—2-Oxy-4:4:6-trimethyltetrahydro-1:3-oxazine,



is formed by the action of ethyl chlorocarbonate on diacetonalkamine in ethereal solution, or by treating the hydrobromide of δ -bromo- β -amino- β -methylpentane (Kahan, Abstr., 1897, i, 494) with silver carbonate in boiling aqueous solution; it crystallises from a mixture

of benzene and light petroleum in white leaflets, melts at 128—131°, and boils at about 301°.

2-Oxy-3 : 4 : 4 : 6-tetramethyltetrahydro-1 : 3-oxazine,



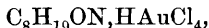
formed by the action of ethyl chlorocarbonate on methyl diacetone-alkamine, crystallises from a mixture of benzene and light petroleum, melts at 84—87°, and boils at about 286°.

The action of ethylene oxide on diacetonealkamine in aqueous solution at 0°, leads to the formation of ethanoldiacetonealkamine and an extremely viscid liquid of high boiling point which may be *diethanol-diacetonealkamine*.

Ethanoldiacetonealkamine, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, forms a colourless, almost odourless, viscid liquid, boils at 154—155° under 13—14 mm. pressure, and is soluble in water; the *platinichloride*, $(\text{C}_8\text{H}_{19}\text{O}_2\text{N})_2, \text{H}_2\text{PtCl}_6$, is obtained as a sandy, crystalline powder or in glistening needles.

The action of ethylene oxide on methyl diacetonealkamine in aqueous solution at 0° leads to the formation of *ethanolmethyl diacetonealkamine*, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, which is obtained as a colourless, odourless, viscid liquid boiling at 146° under 11 mm. pressure; the *platinichloride*, $(\text{C}_9\text{H}_{21}\text{O}_2\text{N})_2, \text{H}_2\text{PtCl}_6$, forms an ochre-coloured precipitate.

Methyl diacetonealkamine aurichloride, $\text{C}_7\text{H}_{17}\text{ON}, \text{HAuCl}_4$, melting at 101—103°, and *dimethyl diacetonealkamine aurichloride*,



melting at 185°, are described.

G. Y.

Hydroxy- β -isohexylamine. MORITZ KOHN (*Monatsh.*, 1905, 26, 951—958. Compare Kohn and Lindauer, *Abstr.*, 1903, i, 73).—Hydroxy- β -isohexylamine is oxidised by chromic acid in boiling sulphuric acid solution with formation of acetone, alanine, and acetic acid.

Hydroxy- β -isohexylamine and propaldehyde condense at the laboratory temperature to form 4 : 6 : 6-trimethyl-2-propyltetrahydro-1 : 3-oxazine, $\text{O} \begin{array}{c} \text{CHPr}^a \cdot \text{NH} \\ \text{CMe}_2 \cdot \text{CH}_2 \end{array} \text{CHMe}$, which is obtained as a colourless, mobile liquid possessing a characteristic ammoniacal odour of spice; it boils at 165—168° under 750 mm. pressure. The *platinichloride*, $(\text{C}_9\text{H}_{19}\text{ON})_2, \text{H}_2\text{PtCl}_6$, forms sheaves of spicular crystals. The *nitroso-derivative*, $\text{C}_9\text{H}_{18}\text{O}_2\text{N}_2$, is obtained as a yellow oil having an odour of musk. With benzaldehyde at 120°, hydroxy- β -isohexylamine condenses to form 2-phenyl-4 : 6 : 6-trimethyltetrahydro-1 : 3-oxazine, $\text{O} \begin{array}{c} \text{CHPh} \cdot \text{NH} \\ \text{CMe}_2 \cdot \text{CH}_2 \end{array} \text{CHMe}$, which is a colourless oil, boiling at 145—146° under 13 mm. pressure. The *platinichloride*, $(\text{C}_{13}\text{H}_{19}\text{ON})_2, \text{H}_2\text{PtCl}_6$, forms nodular crystals; the *nitroso-derivative* is obtained as a viscid oil. When heated with dilute hydrochloric acid in a sealed tube in the water-bath, the oxazine formed from benzaldehyde and hydroxy- β -isohexylamine is hydrolysed with formation of its generators.

G. Y.

Phenylisooxazolone. ALFRED TINGLE (*Amer. Chem. J.*, 1905, **34**, 471—472).—Phenylisooxazolone, recently described by Posner (*Abstr.*, 1905, i, 577) was first prepared by Claisen and Zedel (*Abstr.*, 1891, 468) and subsequently by the author (*Abstr.*, 1900, i, 544). E. G.

Azoxonium Compounds. II. FRIEDRICH KEHRMANN (*Ber.*, 1905, **38**, 2952—2962. Compare *Abstr.*, 1901, i, 484; this vol., i, 949).—The action of *o*-aminophenol on phenanthraquinone in boiling benzene or alcoholic solution leads to the formation of the ψ -base, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N}(\text{OH}) \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \end{matrix} \text{---} \text{O} > \text{C}_6\text{H}_4$, which crystallises in silvery, almost colourless leaflets, melts at 206° , is soluble in glacial acetic acid, forms, in concentrated sulphuric acid, a bluish-violet solution which, on dilution, becomes red and finally yellow, and forms the unstable yellow ψ -base, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C} = \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{O} \end{matrix} > \text{C}_6\text{H}_4$, as a yellow, flocculent precipitate, which gradually changes into the colourless ψ -base. Phenanthraphenazoxonium hydrogen sulphate, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C} = \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{O}(\text{O} \cdot \text{SO}_3\text{H}) \end{matrix} > \text{C}_6\text{H}_4$, is formed when the concentrated sulphuric acid solution of the ψ -base is exposed to moist air; it separates in glistening, violet-crystals, and when heated with alcoholic sulphuric acid is decomposed into *o*-aminophenol and phenanthraquinone.

The *perbromide*, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C} = \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{OBr}_3 \end{matrix} > \text{C}_6\text{H}_4$, is obtained when the ψ -base is treated with bromine in warm nitrobenzene solution as a green, metallic, crystalline precipitate.

ψ -Phenanthraphenazoxine, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{C} = \text{N} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{O} \end{matrix} > \text{C}_6\text{H}_4$, is formed by reduction of the ψ -base with stannous chloride in alcoholic hydrochloric acid solution; it crystallises in yellow needles, forms a yellow solution with green fluorescence, and is rapidly oxidised to the ψ -base when warmed to 80° or dissolved in concentrated sulphuric acid.

Hydroxydihydrophenanthraphenazoxine, $\begin{matrix} \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N}(\text{OH}) \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \end{matrix} \text{---} \text{O} > \text{C}_6\text{H}_4$, is formed when the ψ -base is carefully warmed with phenylhydrazine; it crystallises in glistening, white sheaves of needles, is converted into the ψ -base when heated at 100° , forms a colourless solution in concentrated sulphuric acid, which becomes bluish-violet owing to formation of phenanthraphenazoxonium hydrogen sulphate, and on addition of a drop of dilute hydrochloric acid to the colourless alcoholic solution immediately yields ψ -phenanthraphenazoxine.

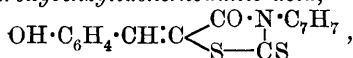
The paper concludes with a criticism of Hantzsch's views as to the constitution of the oxonium dyes (compare Hantzsch, this vol., i, 605). G. Y.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. III. RUDOLF ANDREASCH and ARTHUR ZIPSER (*Monatsh.*, 1905, **26**, 1191—1208. Compare *Abstr.*, 1903, i, 855; 1904, i, 444).—3-*o*-Tolylrhodanic acid, $\text{CH}_2 < \begin{matrix} \text{CO} \cdot \text{N} \cdot \text{C}_6\text{H}_7 \\ | \\ \text{S} \text{---} \text{CS} \end{matrix}$, prepared by

the action of ethyl chloroacetate on ammonium *o*-tolylthiocarbamate, or by boiling *o*-tolylthiocarbimide with thioglycollic acid in aqueous-alcoholic solution, crystallises from alcohol in white or light yellow needles, melts at 101° , and dissolves readily in alcohol, ether, glacial acetic acid, or acetone.

3-o-Tolyl-5-benzylidenerhodanic acid, $\text{CHPh}:\text{C} \begin{smallmatrix} \text{CO}\cdot\text{N}\cdot\text{C}_7\text{H}_7 \\ \text{S}-\text{CS} \end{smallmatrix}$, crystallises in slender needles and melts at 171° .

3-o-Tolyl-5-o-hydroxybenzylidenerhodanic acid,



crystallises in nodular aggregates of light yellow needles, sinters at 150° and melts at 158° ; it dissolves in aqueous ammonia to form a red solution which on warming yields an odour resembling that of phenylthiocarbimide.

3-p-Tolylrhodanic acid, $\text{C}_{10}\text{H}_9\text{ONS}_2$, prepared by the action of ethyl chloroacetate on ammonium *p*-tolylthiocarbamate, crystallises in slender, light yellow needles and melts at 160° .

3-p-Tolyl-5-benzylidenerhodanic acid, $\text{C}_{17}\text{H}_{13}\text{ONS}_2$, crystallises in matted, slender, chrome-yellow needles and melts at $187\cdot5^{\circ}$. *3-p-Tolyl-5-o-hydroxybenzylidenerhodanic acid*, $\text{C}_{17}\text{H}_{13}\text{O}_2\text{NS}_2$, crystallises in microscopic, chrome-yellow needles, melts at 198° , and imparts a yellow colour to fats, but, owing to its insolubility in water, does not dye fibres. It dissolves in aqueous ammonia to form a red solution which, when warmed, gives an odour of tolylthiocarbimide, and on acidification yields a substance crystallising in slender, white needles; with ferric chloride and ammonia, the acidified solution gives an emerald-green coloration.

3-m-Xylylrhodanic acid, $\text{CH}_2 \begin{smallmatrix} \text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}_2 \\ \text{S}-\text{CS} \end{smallmatrix}$, prepared by treat-

ing with ethyl chloroacetate the crystalline product obtained by the action of concentrated aqueous ammonia on a mixture of *m*-xylylidine and carbon disulphide, forms a brownish-yellow oil, which is easily soluble in alcohol or ether. *3-m-Xylyl-5-benzylidenerhodanic acid*,

$\text{CHPh}:\text{C} \begin{smallmatrix} \text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}_2 \\ \text{S}-\text{CS} \end{smallmatrix}$, crystallises in chrome-yellow needles, melts

at 171° , and is readily soluble in warm organic solvents. *3-m-Xylyl-5-m-nitrobenzylidenerhodanic acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C} \begin{smallmatrix} \text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}_2 \\ \text{S}-\text{CS} \end{smallmatrix}$, forms a viscid oil which crystallises in yellow needles when treated with alcohol.

3-o-Hydroxyphenylrhodanic acid, $\text{CH}_2 \begin{smallmatrix} \text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH} \\ \text{S}-\text{CS} \end{smallmatrix}$, is formed

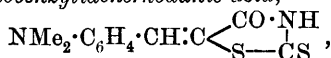
by the action of ethyl chloroacetate on the crystalline product obtained by treating a mixture of *o*-aminophenol and carbon disulphide with concentrated aqueous ammonia. It separates from alcohol as a colourless or slightly yellowish-green, crystalline powder, commences to sinter at 160° , melts at 185° , is readily soluble in alcohol, ether, or acetone, and dissolves in aqueous alkali hydroxides to form solutions which, on acidification, yield a crystalline precipitate and with ferric chloride

and ammonia give the thioglycollic acid reaction. 3-*o*-Hydroxyphenyl-5-benzylidenerhodanic acid, $\text{CHPh}:\text{C} \begin{smallmatrix} \text{CO} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ \text{S} - \text{CS} \end{smallmatrix}$, crystallises in golden-yellow leaflets and melts at 211° .

5-Furfurylidenerhodanic acid, $\text{C}_4\text{OH}_3 \cdot \text{CH}:\text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{S} - \text{CS} \end{smallmatrix}$, on slow crystallisation from alcohol, forms nodules and stellate aggregates of dark brown needles having a steel-blue lustre, commences to sinter at 204° , and decomposes without melting.

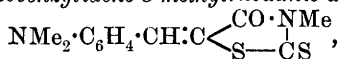
3-Phenyl-5-furfurylidenerhodanic acid, $\text{C}_4\text{OH}_3 \cdot \text{CH}:\text{C} \begin{smallmatrix} \text{CO} \cdot \text{NPh} \\ \text{S} - \text{CS} \end{smallmatrix}$, crystallises from glacial acetic acid in chrome-yellow needles, or in matted, hair-like needles from alcohol, and melts at 183° .

5-*p*-Dimethylaminobenzylidenerhodanic acid,



separates from alcohol as a dark red, crystalline powder, commences to sinter at 200° , decomposes and melts at 246° , and dissolves in alcohol or concentrated acids to form yellow solutions.

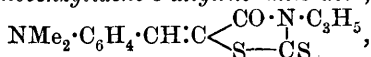
5-*p*-Dimethylaminobenzylidene-3-methylrhodanic acid,



separates from alcohol as a red, shimmering, crystalline powder or in scales, melts at 220° , forms red solutions in alcohol, ether, or acetone, and dissolves in concentrated hydrochloric acid to form a yellow solution which becomes red on dilution.

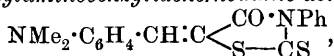
5-*p*-Dimethylaminobenzylidene-3-ethylrhodanic acid, $\text{C}_{14}\text{H}_{16}\text{ON}_2\text{S}_2$, crystallises in dark red scales and melts at 155° .

5-*p*-Dimethylaminobenzylidene-3-allylrhodanic acid,



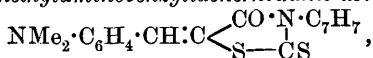
crystallises in small, scarlet leaflets and scales, melts at 131° , is slightly soluble in boiling alcohol, and dyes wool an orange-red, which is bleached by fourteen days' exposure to light.

3-Phenyl-5-dimethylaminobenzylidenerhodanic acid,



separates from alcohol as a red, crystalline powder, melts at 235° , and is most easily soluble in acetone.

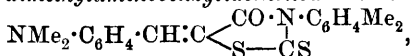
3-*o*-Tolyl-5-*p*-dimethylaminobenzylidenerhodanic acid,



crystallises in yellowish-red needles having a slight blue lustre and melts at 209° .

3-*p*-Tolyl-5-*p*-dimethylaminobenzylidenerhodanic acid, $\text{C}_{19}\text{H}_{18}\text{ON}_2\text{S}_2$, crystallises in delicate, orange-yellow needles and melts at 206° .

3-*m*-Xylol-5-*p*-dimethylaminobenzylidenerhodanic acid,



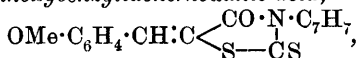
crystallises in light orange-red needles, commences to sinter at 180°, and is completely melted at 200°.

When coupled with diazo-compounds, hydroxybenzylidenerhodanic acid forms derivatives which dye silk and wool directly fast yellow or orange-yellow colours. G. Y.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. IV. JOSEF STUCHETZ (*Monatsh.*, 1905, **26**, 1209—1216. Compare preceding abstract).—3-o-Tolyl-5-m-nitrobenzylidenerhodanic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{CO} \cdot \text{N} \cdot \text{C}_7\text{H}_7 \\ | \\ \text{S} - \text{CS} \end{smallmatrix}$, forms a chrome-yellow, crystalline powder, melts at 193°, and is readily soluble in hot alcohol or cold acetone.

3-o-Tolyl-5-p-nitrobenzylidenerhodanic acid, $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_2\text{S}_2$, crystallises in chrome-yellow, glistening leaflets, commences to blacken at 24°, and melts at 260°.

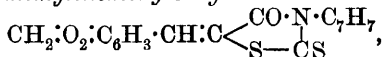
3-o-Tolyl-5-p-methoxybenzylidenerhodanic acid,



crystallises in greenish-yellow needles, melts at 208—212°, and is sparingly soluble in hot alcohol or ether, but easily so in acetone.

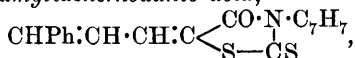
3-o-Tolyl-5-m-methoxybenzylidenerhodanic acid, $\text{C}_{18}\text{H}_{15}\text{O}_3\text{NS}_2$, forms a chrome-yellow, crystalline powder and melts at 168°.

3-o-Tolyl-5-mp-methylenedioxybenzylidenerhodanic acid,



crystallises in greenish-yellow needles and melts at 190°.

3-o-Tolyl-5-cinnamylidenerhodanic acid,



crystallises in glistening, orange-red needles, melts at 175°, and is readily soluble in ether or acetone.

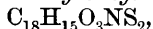
3-o-Tolyl-5-furfurylidenerhodanic acid, $\text{C}_4\text{OH}_3 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{CO} \cdot \text{N} \cdot \text{C}_7\text{H}_7 \\ | \\ \text{S} - \text{CS} \end{smallmatrix}$,

crystallises from alcohol in long, brown needles having a blue lustre and melts at 144°.

3-p-Tolyl-5-p-nitrobenzylidenerhodanic acid, $\text{C}_{17}\text{H}_{12}\text{O}_3\text{N}_2\text{S}_2$, forms glistening, orange-yellow scales and melts at 201°.

3-p-Tolyl-5-p-methoxybenzylidenerhodanic acid, $\text{C}_{18}\text{H}_{15}\text{O}_2\text{NS}_2$, forms a greenish-yellow, crystalline powder and melts at 170°.

3-p-Tolyl-5-p-hydroxy-m-methoxybenzylidenerhodanic acid,



forms a yellow, crystalline powder and melts at 202°.

3-p-Tolyl-5-mp-methylenedioxybenzylidenerhodanic acid, $\text{C}_{18}\text{H}_{13}\text{O}_3\text{NS}_2$, forms a sparingly soluble, chrome-yellow, crystalline powder and melts at 197°.

3-p-Tolyl-5-cinnamylidenerhodanic acid, $\text{C}_{18}\text{H}_{14}\text{ONS}_2$, forms a dark orange-yellow powder, consisting of microscopic needles, and melts at 185°.

3-*p*-Tolyl-5-furfurylidenerhodanic acid, $C_{15}H_{12}O_2NS_2$, forms a greenish-yellow, crystalline powder, melts at 186° , and is moderately soluble in boiling alcohol. G. Y.

Action of Sulphuric Acid on Diphenylamine. VICTOR KADIERA (*Ber.*, 1905, 38, 3575—3578. Compare Gnehm and Werdenberg, *Abstr.*, 1900, i, 93. Ullmann, *Abstr.*, 1903, i, 692).—When heated at 80° with 1 part of concentrated sulphuric acid and 3 parts of sulphuric acid containing 20 per cent. of anhydride, diphenylamine yields 37.5 per cent. of its weight of diphenylbenzidine, together with diphenylbenzidinesulphone.

Diphenylbenzidine, $NHPh \cdot C_6H_4 \cdot C_6H_4 \cdot NHPh$, crystallises from toluene in white leaflets, melts at 242° (corr.), is readily soluble in boiling toluene or acetic acid, but only sparingly so in benzene, acetone, or alcohol, and dissolves in cold concentrated sulphuric acid to form a colourless solution which becomes intensely blue when heated, or on addition of a small quantity of potassium nitrate; the yellow solution in acetic acid becomes blue on addition of potassium dichromate, greenish-yellow on addition of ferric chloride.

Diphenylbenzidinedicarboxylic acid, $C_{12}H_8(NH \cdot C_6H_4 \cdot CO_2H)_2$, is formed when *o*-chlorobenzoic acid is boiled with benzidine and potassium carbonate in amyl alcohol solution, in presence of copper powder, in a reflux apparatus. It crystallises from boiling alcohol as a delicate, yellowish-green powder, melts and decomposes at 278° (corr.), and at 285° loses carbon dioxide and yields diphenylbenzidine.

Diphenylbenzidinesulphone,
$$NHPh \cdot \overset{\overset{CH \cdot CH : C}{\parallel}}{\underset{\underset{CH : C \cdot NHPh}{\parallel}}{C}} \cdot SO_2 \cdot \overset{\overset{C \cdot CH : CH}{\parallel}}{\underset{\underset{CH : C \cdot NHPh}{\parallel}}{C}}$$
 crystallises from amyl alcohol as a yellowish-brown powder, does not melt at 300° , forms solutions with slight blue fluorescence in amyl alcohol and aniline, and gives colour reactions similar to those of diphenylbenzidine. G. Y.

Coloured and Colourless Di-imines. HANS H. PRINGSHEIM (*Ber.*, 1905, 38, 3354—3356. Compare Jackson and Calhane, *Abstr.*, 1902, i, 645; Willstätter, *ibid.*, 1904, i, 511; this vol., i, 723).—A résumé of earlier work. J. J. S.

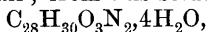
Indophenols containing the Sulphamino-group. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 160710).—Indophenols containing the sulphamino-group, of which the simplest representative has the constitution $O : C_6H_4 : N \cdot C_6H_4 \cdot NH \cdot SO_2Ph$, are obtained by oxidising an arylsulphonyl-*p*-phenylenediamine together with a phenol in which the *para*-position is free. Thus, on oxidising a mixture of toluene-*p*-sulphonyl-*p*-phenylenediamine hydrochloride and phenol with chromic acid, the *indophenol* is obtained as a reddish-brown precipitate, insoluble in water, but dissolving in alkali hydroxides or carbonates to an intensely blue solution. The phenol may be replaced by *o*- or *m*-cresol or α -naphthol, and the amine by toluene-*p*-sulphonyl-*o*-chloro-*p*-phenylenediamine or toluene-*p*-sulphonyl-*om*-tolylene-diamine.

C. H. D.

Rhodamines. I. EMILIO NOELTING and KARL DZIEWOŃSKI (*Ber.*, 1905, 38, 3516—3527).—A typical rhodamine is produced when *o*'-amino-*o*-cresol, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$ [2 : 1 : 6], is condensed with phthalic anhydride under the conditions which convert *m*-aminophenol into the simplest rhodamine, thus proving that the OH or NH_2 group in fluorescein and the rhodamines is in the para-position to the fundamental carbon atom.

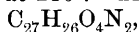
Tetramethylrhodamine yields a *hydrochloride*, $\text{C}_{24}\text{H}_{23}\text{O}_3\text{N}_2\text{Cl}\cdot 3\text{H}_2\text{O}$, which forms green needles with a metallic lustre. The *tetramethyl-rhodamine base*, $\text{C}_{24}\text{H}_{22}\text{O}_3\text{N}_2\cdot 3\text{H}_2\text{O}$, is insoluble in water and in excess of alkali hydroxide, but separates from hot alcohol in green flakes with a metallic lustre; it loses water of crystallisation at $120\text{--}130^\circ$, gives a colourless solution in ether, benzene, toluene, or xylene, and separates from the latter in flat, colourless needles with C_8H_{10} , which is evolved at $130\text{--}150^\circ$, the base melting at 232° .

Tetraethylrhodamine hydrochloride, $\text{C}_{28}\text{H}_{31}\text{O}_3\text{N}_2\text{Cl}$, crystallises from dilute hydrochloric acid in scales with a metallic lustre and dissolves in alcohol very easily to a carmine-red solution with an orange-yellow fluorescence. Addition of concentrated alkali to a solution of the hydrochloride yields a reddish-white precipitate, which readily dissolves on diluting the alkali; from this solution, the *base*,



separates in glistening, green scales. It dissolves in water and in alcohol to red solutions with a green fluorescence, but yields colourless solutions in ether, benzene, xylene, &c. The green base loses water when kept in a vacuum over sulphuric acid; it becomes colourless when heated at $70\text{--}80^\circ$, melts at 95° , solidifies again, and melts at 165° to a clear red liquid. The colourless *anhydrous base* separates from absolute alcohol in large, almost colourless prisms, and melts at 165° ; it separates from xylene in colourless prisms with C_8H_{10} , which is eliminated at $140\text{--}150^\circ$.

Diethylhomorhodamine hydrochloride, $\text{C}_{25}\text{H}_{25}\text{O}_3\text{N}_2\text{Cl}\cdot 3\text{H}_2\text{O}$, separates from dilute hydrochloric acid in green prisms with a metallic lustre, dissolves in alcohol with a yellow fluorescence, and becomes anhydrous when kept in a vacuum over sulphuric acid. The *base*, $\text{C}_{25}\text{H}_{24}\text{O}_3\text{N}_2$, separates from dilute alcohol in glistening, green scales with EtOH and H_2O ; it gives a colourless solution in xylene and separates in red plates, with a golden lustre, containing xylene, which is lost at $170\text{--}175^\circ$, the base melting at 210° . The *acetyl derivative*,



separates from benzene or xylene, in small, white needles and melts at $257\text{--}260^\circ$.

The *hydrochloride* of *s*-diethylrhodamine, $\text{C}_{24}\text{H}_{23}\text{O}_3\text{N}_2\text{Cl}\cdot 3\frac{1}{2}\text{H}_2\text{O}$, forms brownish-red needles with a metallic lustre. The *base*, $\text{C}_{24}\text{H}_{22}\text{O}_3\text{N}_2\cdot \text{H}_2\text{O}$, forms bluish-red, glistening, rhombic plates; it separates from xylene with $\frac{1}{2}\text{H}_2\text{O}$ in dark red, bulky crystals. The *diacetyl derivative*, $\text{C}_{28}\text{H}_{26}\text{O}_5\text{N}_2$, crystallises from a mixture of xylene and light petroleum in small, colourless prisms and melts at 205° .

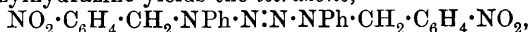
apoRhodamine (aminofluorene) hydrochloride, $\text{C}_{23}\text{H}_{20}\text{O}_3\text{NCl}\cdot 2\frac{1}{2}\text{H}_2\text{O}$, forms brownish-red needles and yields the free, colourless base, when boiled with water. The colourless base, $\text{C}_{23}\text{H}_{19}\text{O}_3\text{N}$, separates from

ether, alcohol, or benzene in large, flat, glistening, colourless needles, and from xylene in small, colourless prisms containing xylene, which is given off at 180—185°; the base melts at 197°.

T. M. L.

Action of Benzyl Chloride and *o*- and *p*-Nitrobenzyl Chlorides on Phenylhydrazine and *p*-Bromophenylhydrazine. OTTO FLASCHNER (*Monatsh.*, 1905, 26, 1069—1090. Compare Paal and Bodewig, Abstr., 1892, 1455; Ofner, Abstr., 1904, i, 818).—The action of 2 mols. of phenylhydrazine on 1 mol. of *o*-nitrobenzyl chloride in boiling alcoholic solution leads to the formation of *as*-phenyl-*o*-nitrobenzylhydrazine, phenyl-*o*-nitrobenzylidenehydrazine, which melts at 154° and is identical with Paal and Bodewig's *o*-nitrophenylmethane-azobenzene, and phenyl *o*-nitrobenzyl-*o*-nitrobenzylidenehydrazine, which melts at 126°. This substance, which is identical with Paal and Bodewig's bisphenyl-*o*-nitrobenzylhydrazine, is formed also by condensation of *o*-nitrobenzaldehyde with phenyl-*o*-nitrobenzylhydrazine.

When oxidised with aqueous ferric chloride under cooling, *as*-phenyl-*o*-nitrobenzylhydrazine yields the *tetrazone*,



which crystallises in flat, yellow prisms and decomposes at 174—175° (corr.), but, when oxidised with mercuric oxide, it forms phenyl-*o*-nitrobenzylidenehydrazine.

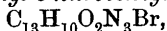
The reduction product of phenyl-*o*-nitrobenzylidenehydrazine, which melts at 218—220° (Paal and Bodewig), is identical with phenyl-*o*-aminobenzylidenehydrazine (Gabriel and Leupold, Abstr., 1899, i, 85).

The action of *p*-nitrobenzyl chloride on phenylhydrazine in boiling alcoholic solution leads to the formation of (1) *phenyl-p-nitrobenzylhydrazine*, $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3$, which crystallises from alcohol in yellow prisms, melts at 95° (corr.), and forms a *hydrochloride* crystallising in transparent, white, quadratic prisms and decomposing at 198° (corr.); (2) *phenyl-p-nitrobenzyl-p-nitrobenzylidenehydrazine*, $\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_4$, which is formed also by the action of *p*-nitrobenzaldehyde on phenyl-*p*-nitrobenzylhydrazine, crystallises in needles, and melts at about 132° (corr.), and (3) *phenyl-p-nitrobenzylidenehydrazine*, $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_3$, which is formed also by the interaction of phenylhydrazine and *p*-nitrobenzaldehyde, crystallises in needles, and melts at 159—160° (corr.).

The action of benzyl chloride on *p*-bromophenylhydrazine leads to the formation of *as-p-bromophenylbenzylhydrazine*, $\text{C}_{13}\text{H}_{13}\text{N}_2\text{Br}$, which crystallises in nodular aggregates of transparent, white needles, melts at 37°, and forms a *hydrochloride*, $\text{C}_{13}\text{H}_{13}\text{N}_2\text{Br} \cdot \text{HCl}$, crystallising in needles and decomposing at 182° (corr.), and *p-bromophenylbenzylbenzylidenehydrazine*, $\text{C}_{20}\text{H}_{17}\text{N}_2\text{Br}$, which can be prepared from *p*-bromophenylbenzylhydrazine and benzaldehyde; it crystallises in greenish-yellow leaflets and melts at 134° (corr.).

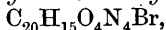
When boiled in alcoholic solution, *o*-nitrobenzyl chloride and *p*-bromophenylhydrazine interact to form *as-p-bromophenyl-o-nitrobenzylhydrazine*, $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_3\text{Br}$, which separates from alcohol in lemon-yellow crystals, melts at 123° (corr.), and forms a *hydrochloride*,

$C_{13}H_{12}O_2N_3Br$, HCl , crystallising in white needles and decomposing at about 190° , and *p*-bromophenyl-*o*-nitrobenzylidenehydrazine,



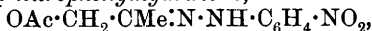
which is formed also by the action of *o*-nitrobenzaldehyde on *p*-bromophenylhydrazine; it crystallises in dark red needles and melts and decomposes at 184 — 189° (corr.).

p-Bromophenyl-*o*-nitrobenzyl-*o*-nitrobenzylidenehydrazine,



is formed by heating *o*-nitrobenzaldehyde with *as*-*p*-bromophenyl-*o*-nitrobenzylhydrazine in alcoholic solution; it crystallises in yellow needles and melts at 167° (corr.). The action of *p*-nitrobenzyl chloride on *p*-bromophenylhydrazine leads to the formation of (1) *as*-*p*-bromophenyl-*p*-nitrobenzylhydrazine, which crystallises in yellow prisms and melts at 144° (corr.); the hydrochloride forms white leaflets and decomposes at 217° ; (2) *p*-bromophenyl-*p*-nitrobenzyl-*p*-nitrobenzylidenehydrazine, $C_{20}H_{15}O_4N_4Br$, which is formed also by the action of *p*-nitrobenzaldehyde on *as*-*p*-bromophenyl-*p*-nitrobenzylhydrazine; it crystallises in scarlet prisms and melts at 182 — 183° (corr.); and (3) *p*-bromophenyl-*p*-nitrobenzylidenehydrazine, $C_{13}H_{10}O_2N_3Br$, which is formed also from *p*-nitrobenzaldehyde and *p*-bromophenylhydrazine; it crystallises in flat, red needles and melts at 154 — 156° (corr.). The *as*-*sec*-hydrazine is always the chief product of the action of benzyl and nitrobenzyl chlorides on phenyl- or bromophenylhydrazine. G. Y.

Nitrogen Derivatives of Acetylcarbinol. F. CARLO PALAZZO and A. CALDARELLA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 151—156).—The *p*-nitrophenylhydrazone,



prepared by the action of a hydrochloric acid solution of *p*-nitrophenylhydrazine on acetylcarbinyl acetate (Perkin, *Trans.*, 1891, 59, 786) in presence of excess of sodium acetate, separates from benzene as a yellow, crystalline powder melting at 144° . The *p*-bromophenylhydrazone, $C_{11}H_{13}O_2N_2Br$, crystallises from light petroleum, benzene, or alcohol in white scales, which melt at 137 — 138° , and when kept rapidly turns into a resin.

Acetylcarbinyl-p-nitrophenylhydrazone, $C_9H_{11}O_3N_3$, separates from xylene as a pale yellow, crystalline powder melting at 190 — 191° . The corresponding *p*-bromophenylhydrazone, $C_9H_{11}ON_2Br$, crystallises from light petroleum, either alone or mixed with benzene, in white leaflets melting at 128 — 130° . T. H. P.

Action of Secondary Asymmetric Hydrazines on Sugar. II. RUDOLF OFNER (*Monatsh.*, 1905, 26, 1165—1190. Compare *Abstr.*, 1904, i, 689, 798, 936; this vol., i, 90, 158).—A reply to Neuberg (this vol., i, 90) and a criticism of Neuberg and Strauss' work (*Abstr.*, 1902, ii, 676). It is probable that the body-juices examined by these authors contain dextrose and not lævulose, as the phenyl-methyllosazone test for the latter sugar is trustworthy only if the osazone separates in about five hours at the ordinary temperature.

G. Y.

Amines and Diazopyrroles. FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 167—170).—The analogy in behaviour between phenols and pyrrole derivatives is supported by the fact that on reduction nitrosophenylindole yields aminophenylindole and nitrosodiphenyl- and nitrosotriphenyl-pyrroles give the corresponding aminopyrroles. The latter behave like the aminoindoles towards nitrous acid, giving rise to extremely stable diazopyrroles.

Aminotriphenylpyrrole, $C_{22}H_{18}N_2$, prepared by reducing an alcoholic solution of nitrosotriphenylpyrrole by means of zinc dust and acetic acid, crystallises from benzene in colourless needles melting and decomposing at $183-184^\circ$.

Aminodiphenylpyrrole, $C_{16}H_{14}N_2$, crystallises from benzene in pale yellow scales melting at $187-188^\circ$.

Diazotriphenylpyrrole, $C_{22}H_{15}N_3$, crystallises from benzene or alcohol in reddish-brown needles melting and decomposing at $158-159^\circ$. Its *hydrochloride*, $C_{22}H_{15}N_3 \cdot HCl$, forms a yellow powder decomposing at about 160° .

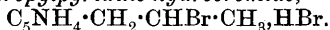
Diazodiphenylpyrrole, $C_{16}H_{11}N_3$, crystallises from benzene in large, reddish-brown needles melting and decomposing at $122-123^\circ$; the *hydrochloride* is a yellow powder decomposing at about 173° .

T. H. P.

Derivatives of 2-Picolyl- and of 2-Picolylmethyl-alkine.

III. KARL LÖFFLER and M. KIRSCHNER (*Ber.*, 1905, 38, 3329—3343. Compare *Abstr.*, 1904, i, 265, 616).—2- β -2'-*Pipecolylethylpyridine*, $C_5NH_4 \cdot C_2H_4 \cdot C_5NH_3Me$, is obtained when 2-picolylalkine bromide is heated with twice its weight of 2-pipecoline and ethyl alcohol at 100° for 5—6 hours. It is a viscid, colourless oil, distils at 152° under 15 mm. pressure, has a sp. gr. 1.0105 at 15° , dissolves readily in most organic solvents, and its aqueous solution is strongly alkaline. It cannot be resolved into active components by means of *d*-tartaric acid or camphorsulphonic acid. The *hydrochloride*, $C_{13}H_{20}N_2 \cdot 2HCl$, melts at 175° , the *aurichloride* melts and decomposes at 190° , the *platinichloride*, $C_{13}H_{20}N_2 \cdot H_2PtCl_6$, crystallises in pale yellow plates and decomposes at $230-232^\circ$, the *picrate* melts at $131-132^\circ$, and the *mercurichloride* at 118° .

2-Picolylmethylalkine (Ladenburg, *Annalen*, 1898, 301, 124), when heated for 12—14 hours at 125° with hydrobromic acid saturated at 0° , yields 1- β -bromopropylpyridine *hydrobromide*,



The base is a yellow oil with an intense odour, and is sparingly soluble in water. The *picrate* crystallises from water in plates and melts at 105° ; the *platinichloride* melts at 170° and the *aurichloride* at $102-103^\circ$. When warmed or when kept, the base undergoes intramolecular transformation

into the *pyridinium bromide*, $\begin{array}{c} CH:CH \cdot C-CH_2 \\ | \\ CH:CH \cdot NBr \cdot CHMe \end{array}$, which crystallises from ethyl acetoacetate in colourless plates melting at 162° , and readily soluble in alcohol, chloroform, or acetone. The *iodide* melts at 147° , the *chloride* is hygroscopic and melts at 122° , and the *platinichloride* forms reddish-yellow needles melting at 188° .

2- β -Diethylaminopropylpyridine, $C_5NH_4 \cdot CH_2 \cdot CHMe \cdot NEt_2$, obtained by the action of diethylamine on the corresponding bromo-derivative

at 120—125°, is an oil which distils at 122° under 12 mm. pressure. It dissolves readily in most solvents, the *picrate* melts at 108°, the *platinichloride*, $C_{12}H_{20}N_2, H_2PtCl_6$, crystallises in orange-yellow needles and melts at 190°, the *aurichloride* melts at 160°, and the *mercurichloride* at 110°.

2- β -Ethylaminopropylpyridine, $C_5NH_4 \cdot CH_2 \cdot CHMe \cdot NHEt$, distils at 108—109° under 13 mm. pressure, has a sp. gr. 0.9533, darkens in contact with air, and is extremely hygroscopic. The *platinichloride* crystallises in red, well-developed prisms melting and decomposing at 225°. The *aurichloride* melts at 204°, the *mercurichloride* at 146°, and the *picrate* at 178°. The base yields a nitroso-derivative in the form of a red oil, which is soluble in mineral acids and which yields a *platinichloride* crystallising in orange-yellow needles and melting at 198°.

2- β -Aminopropylpyridine, $C_5NH_4 \cdot CH_2 \cdot CHMe \cdot NH_2$, distils at 103—104° under 13 mm. pressure and has a sp. gr. 1.004 at 15°. It cannot be resolved by means of tartaric or camphorsulphonic acid. The *aurichloride* melts and decomposes at 216° and the *platinichloride* at 239°. The *mercurichloride* melts at 122° and the *picrate* at 210—211°.

The bromide obtained by the action of hydrobromic acid on 2-pipecolylalkine also reacts with bases. 2- β -Diethylaminoethylpiperidine, $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot NEt_2$, is a colourless oil distilling at 113—115° under 15 mm. pressure and has a sp. gr. 0.8288 at 15°. The *platinichloride* crystallises in glistening, yellow plates decomposing at 224°. The *hydrochloride*, $C_{11}H_{24}N_2, 2HCl$, melts at 256—258°, the *hydrobromide* at 236°, the *aurichloride* at 193°, the *picrate* at 73°, and the *cadmium salt* at 163°.

2- β -Ethylaminoethylpiperidine, $C_5NH_{10} \cdot CH_2 \cdot CH_2 \cdot NHEt$, is a colourless, basic oil distilling at 95—96° under 10 mm. pressure. The *aurichloride* melts at 186°, the *platinichloride* decomposes at 196°, and the *picrate* crystallises in pale yellow needles melting at 170°. Amino-2-ethylpiperidine is not prepared so readily as its ethyl derivatives. It distils at 106—107° under 10 mm. pressure and its aqueous solution is strongly alkaline. The *picrate* and *mercurichloride* are oils.

2-Pipecolylmethylalkine also reacts with fuming hydrobromic acid and phosphorus at 145—150°, yielding the *hydrobromide* of the bromo-base, $C_5NH_{10} \cdot CH_2 \cdot CHBr \cdot CH_3$. The *hydrobromide* melts at 148—150° and the *hydrochloride* at 135—136°. The *aurichloride* and *picrate* are oils. The bromo-base reacts with amines.

2- β -Diethylaminopropylpiperidine, $C_5NH_{10} \cdot CH_2 \cdot CHMe \cdot NEt_2$, is a colourless oil distilling at 113—115° under 14 mm. pressure and readily soluble in alcohol or ether. It has a sp. gr. 0.8954. The *platinichloride*, $C_{12}H_{26}N_2, H_2PtCl_6$, melts and decomposes at 208°; the *aurichloride* melts at 180—181° and the *picrate* is an oil.

Conhydrine also reacts with fuming hydrobromic acid and red phosphorus at 140—150°, yielding the *hydrobromide*, $C_8H_{16}NBr, HBr$, which crystallises from alcohol in colourless needles melting at 183—185°. The *base* is oily and has an alliaceous odour. The *picrate* and *aurichloride* are oils; the *platinichloride* melts and decomposes at 182°. When heated with excess of diethylamine, the bromo-base yields *diethylaminoconiine*, $C_5NH_{10} \cdot C_3H_6NEt_2$, which distils at

112—115° under 13 mm. pressure and has a sp. gr. 0.8970 at 15° and $[\alpha]_D - 5.82^\circ$. It closely resembles the inactive base obtained from the bromo-derivative of pipecolylmethylalkine. The *platinichloride* decomposes at 227° and the *aurichloride* at 181°. The *picrate* and *cadmium* salt are oils.

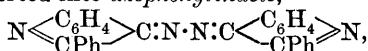
Ethylaminoconiine distils at 105° under 16 mm. pressure, has a sp. gr. 0.9001 at 15°, and is inactive. The *aurichloride* melts at 156—157°; the *platinichloride* melts and decomposes at 221—222°; the *picrate* is extremely readily soluble in alcohol. *Aminoconiine* distils at 95—99° under 15 mm. pressure, has a sp. gr. 0.9942 at 15°, and $[\alpha]_D - 2.33^\circ$. Hofmann and Lellmann's ϵ -coniceine (Abstr., 1885, 401; 1890, 1328) is obtained as a by-product in the action of amines on the bromide from conhydrine. It has $[\alpha]_D + 37^\circ$. An inactive isomeride is also formed by the action of diethylaniline on the bromide from 2-pipecolylmethylalkine.

J. J. S.

Diazoindoles. V. CASTELLANA and ANTONINO D'ANGELO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 145—151. Compare Angeli and d'Angelo, Abstr., 1904, i, 537, and Angeli, *Gazzetta*, 1893, 23, ii, 345).—On reduction with zinc dust and acetic acid, the ethyl derivative of 3-nitroso-2-phenylindole gives 3-amino-2-phenylindole, which with nitrous acid yields diazophenylindole. The ethyl derivative of 3-nitrophenylindole or of 3-nitromethylindole, on the other hand, yields 1-ethylaminophenylindole or 1-ethylaminomethylindole, and no diazo-compound is obtained with nitrous acid, because no hydrogen is attached to the carbon atom bearing the amino-group and no mobile hydrogen to the nitrogen atom. It is hence assumed that, when the diazo-compound is obtained, the aminophenylindole behaves as the tautomeride having the structure $C_6H_4 \begin{smallmatrix} \text{CH}(\text{NH}_2) \\ \text{N} \end{smallmatrix} \gg CPh$. These diazo-compounds are very stable, probably owing to the diazo-group being between two substituents in the ortho-position.

3-Nitroso-2-phenylindole ethyl ether, $C_{16}H_{14}ON_2$, crystallises from light petroleum in orange-red needles melting at 91°.

Diazophenylindole, $C_{14}H_9N_3$, crystallises from light petroleum in intensely orange-yellow, unstable prisms having a characteristic odour and melting at 115°. The *picrate*, $C_{20}H_{12}O_7N_6$, crystallises from alcohol in yellow needles melting and decomposing at 155°; the *hydrochloride*, $C_{14}H_9N_3 \cdot HCl$, forms yellow needles melting at 173°; the *nitrate*, $C_{14}H_9N_3 \cdot HNO_3$, separates from water in crystals decomposing at 164—165°; the *chromate*, $C_{14}H_9N_3 \cdot CrO_3$, separates from water in large, yellow crystals melting at about 255°. On reduction in ethereal solution with aluminium amalgam, diazophenylindole yields nitroso-phenylindole, and by prolonged boiling with 25 per cent. sulphuric acid solution it is converted into *azophenylindole*,



which crystallises from xylene in yellowish-red scales decomposing at about 180°, and on reduction yields aminophenylindole.

Reduction of the ethyl derivative of 3-nitro-2-methylindole yields a

compound which does not give a diazo-compound on treatment with nitrous acid, but forms a *picrate*, $C_{17}H_{17}O_7N_5$, melting at $180-182^\circ$.

Diazomethylindole, $C_9H_7N_3$, separates from light petroleum in dark yellow, unstable crystals melting at 94° . Its *picrate*, $C_{15}H_{10}O_7N_6$, crystallises from alcohol in yellow needles melting at 172° ; its *iodide*, $C_9H_7N_3I_2$, forms a brown, crystalline precipitate decomposing at about 80° ; the *hydrochloride*, $C_9H_7N_3 \cdot 2HCl$, is obtained as a brown, crystalline precipitate decomposing at about 100° . T. H. P.

Pyrazoline Ketones. E. AZZARELLO (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 229—234. Compare von Pechmann, *Abstr.*, 1894, i, 438; 1895, i, 328; 1899, i, 232; 1901, i, 167, 168).—By the action of diazomethane on unsaturated ketones containing the group $\cdot CH:CH \cdot CO \cdot$ or $\cdot CH:CH \cdot CO \cdot CH:CH \cdot$, the following compounds have been obtained.

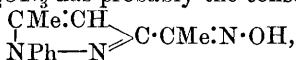
5(or 3)-*Acetyl-4-phenylpyrazoline*, $CH \begin{smallmatrix} \text{CHPh} \\ \text{N} \cdot \text{NH} \end{smallmatrix} CHAc$, prepared by the action of diazomethane on benzylideneacetone in ethereal solution, crystallises from alcohol in white needles melting at $105-106^\circ$ and is soluble in chloroform, ether, acetone, or benzene, and slightly so in light petroleum or water; it turns red in the air, decolorises alkaline permanganate solution instantly, gives red colorations with acids, is resinified by picric acid in alcoholic solution, and, in alcoholic solution containing a little water, forms more or less unstable precipitates with platinic or mercuric chloride or ammoniacal silver nitrate solution. The *oxime*, $C_8H_4N_2Ph \cdot CMe:N \cdot OH$, separates in minute, shining crystals melting at $181-182^\circ$, dissolves in alcohol, ether, or acetone, and with concentrated sulphuric acid gives a violet-red coloration with yellow edges. Oxidation of 5(or 3)-acetyl-4-phenylpyrazoline in chloroform solution with bromine and subsequently with potassium permanganate yields 4-phenylpyrazole-5(or 3)-carboxylic acid (compare Knorr, *Abstr.*, 1895, i, 396) and Pechmann (*loc. cit.*).

Phenylpyrazoline ketone, $CO(C_6H_4N_2Ph)_2$, prepared by the interaction of dibenzylideneacetone and diazomethane in ethereal solution, is a yellow substance melting at $214-216^\circ$, and is mixed with a small quantity of a yellow, crystalline, isomeric compound melting at $174-176^\circ$. T. H. P.

Transformation of Pyrroles into Derivatives of Pyrazole.

V. CASTELLANA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 242—244).—On boiling an alcoholic solution of benzeneazo-2:5-dimethylpyrrole for some hours with sodium hydroxide and hydroxylamine, it yields a compound, $C_{12}H_{13}ON_3$, which crystallises from benzene in minute, yellow needles melting at 175° . Its *benzoyl* derivative, $C_{19}H_{17}O_2N_3$, separates from light petroleum in yellow crystals melting at 156° . On boiling the compound with dilute sulphuric acid solution, it is converted into a ketone, $\begin{smallmatrix} CMe:CH \\ NPh-N \end{smallmatrix} > C \cdot COMe$ (?), which crystallises from light petroleum in long, almost white needles melting at 90° .

The compound $C_{12}H_{13}ON_3$ has probably the constitution



so that hydroxylamine acts on benzeneazo-2:5-dimethylpyrazole in the same manner as it does on the pyrroles and nitrosopyrroles.

T. H. P.

1-Phenyl-4-methylpyrazolone. FRIEDRICH STOLZ (*Ber.*, 1905, 38, 3273—3276. Compare Michael, this vol., i, 564)—1-Phenyl-4-methyl-5-pyrazolone, melting at 148° , is formed from 1-phenyl-4-methyl-5-pyrazolone-3-carboxylic acid by removal of carbon dioxide. In Fichter, Enzenauer, and Uellenberg's paper (*Abstr.*, 1900, i, 312), the nomenclature of the 1-phenyl-4-methyl-5-pyrazolone and 1-phenyl-4-methyl-3-pyrazolone must be interchanged; the substance termed 2-acetyl-1-phenyl-4-methyl-3-pyrazolone, and melting at 167° , is 5-acetoxy-1-phenyl-4-methylpyrazole. A number of 1-phenyl-5-pyrazolone and the corresponding 1-phenyl-3-pyrazolone derivatives are quoted to show that the latter melt always at the higher temperature. When heated with methyl iodide and methyl alcohol in a sealed tube for six hours in the water-bath, 1-phenyl-4-methyl-5-pyrazolone forms 1-phenyl-2:4-dimethyl-5-pyrazolone, $C_{11}H_{12}ON_2$, which crystallises from benzene in colourless prisms, or from water in glistening prisms containing $2H_2O$, melts when anhydrous at 125° , is less soluble in water than is antipyrine, and forms precipitates with picric acid and ferrocyanic acid; it is obtained also by decomposition of methylantipyrine.

G. Y.

5-Methylpyrimidine. OTTO GERNGROSS (*Ber.*, 1905, 38, 3394—3408).—Details are given for preparing C-methylbarbituric acid from ethyl isosuccinate. 2:4:6-Trichloro-5-methylpyrimidine, $\text{CCl} \begin{array}{c} \text{N} \cdot \text{CCl} \\ \text{N} \cdot \text{CCl} \end{array} \text{CMe}$, prepared by heating the sodium derivative of methylbarbituric acid with phosphorus oxychloride for 2—3 hours at 120° , crystallises from water in thin, rhombic plates, melts at $67.5\text{--}68^\circ$, boils at 245.5° under 748 mm. pressure, and when heated with zinc dust and water gives rise to a mixture of 5-methylpyrimidine, $\text{CH} \begin{array}{c} \text{N} \cdot \text{CH} \\ \text{N} \cdot \text{CH} \end{array} \text{CMe}$, and 2-chloro-5-methylpyrimidine. The former crystallises in flat, lustrous needles, melts at 30.5° , boils at 151.5° under 735 mm. pressure, and gives a mercurichloride melting at 246° , a picrate melting at 141° , and an aurichloride which melts at 209° . 2-Chloro-5-methylpyrimidine crystallises from water in soft, colourless needles, melts at 92.5° , and gives a mercurichloride melting at 219° ; its structure follows from its giving 2-amino-5-methylpyrimidine, $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{CH} \\ \text{N} \cdot \text{CH} \end{array} \text{CMe}$, when heated with alcoholic ammonia for three hours at 200° . This substance crystallises from hot water in four-sided prisms, melts at 193.5° , gives a platinichloride which decomposes at 255° , and may be synthesised as follows. isoSuccinylguanidine, $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{C}(\text{OH}) \\ \text{N} \cdot \text{C}(\text{OH}) \end{array} \text{CMe}$, obtained by condensing ethyl

isosuccinate with guanidine thiocyanate by means of sodium in absolute alcohol, crystallises from water in thin, rhombic, nacreous plates, does not melt at 300° , and when heated with phosphorus oxychloride gives 4:6-dichloro-2-amino-5-methylpyrimidine; this sublimes in a vacuum in well-formed prisms, melts at 249° , and on reduction with zinc dust and water gives the 2-amino-5-methylpyrimidine described above.

Ammonia at the ordinary temperature converts 2:4:6-trichloro-5-methylpyrimidine dissolved in absolute alcohol into 2:4-dichloro-6-amino-5-methylpyrimidine, which crystallises from water in long, thin needles, melts at 201° , and can be sublimed; it is not reduced when boiled with zinc dust and water, but with hydriodic acid readily gives 6-iodo-4-amino-5-methylpyrimidine, which crystallises from water in thin, four-sided plates, melts at 238° , and gives a *hydriodide* melting at 227° . On reduction with zinc dust and water, 4-amino-5-methylpyrimidine is obtained, which melts at 176° and gives a *picrate* melting at $219-221^{\circ}$. 4:6-Diamino-5-methylpyrimidine is obtained by heating 6-iodo-4-amino-5-methylpyrimidine with alcoholic ammonia for three hours at 210° ; it is purified by distillation in a vacuum, melts at 243° , and crystallises from water in large, colourless needles; the *hydrochloride* sublimes in a vacuum, the *platinichloride* decomposes at $265-266^{\circ}$, and the *nitrate* decomposes at 276° .

6-Chloro-2:4-diamino-5-methylpyrimidine is prepared by heating 2:4:6-trichloro-5-methylpyrimidine with alcoholic ammonia at 160° ; it crystallises from water in quadrangular plates, melts at $199-200^{\circ}$, and gives a *nitrate* which decomposes at 202° and a crystalline *platinichloride* which decomposes at 300° . The same base is obtained by heating either 4:6-dichloro-2-amino-5-methylpyrimidine or 2:6-dichloro-4-amino-5-methylpyrimidine with alcoholic ammonia at 160° .

On reduction with boiling hydriodic acid and red phosphorus, 2:4-diamino-5-methylpyrimidine is formed; it crystallises from alcohol or ethyl acetate in aggregates of large prisms, melts at $188-189^{\circ}$, and gives a *nitrate* which decomposes at 231° and a *platinichloride* which decomposes at 246° .

2:4:6-Triamino-5-methylpyrimidine is obtained by heating 2:4:6-trichloro-5-methylpyrimidine with alcoholic ammonia at 200° ; it melts at $227-228^{\circ}$ and gives a *nitrate*, $C_5H_9N_5 \cdot 2HNO_3$, which decomposes 168° and 178° ; the *platinichloride* has the composition $C_5H_9N_5 \cdot H_2PtCl_6$.
W. A. D.

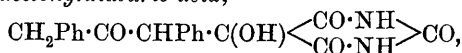
A Synthesis of Thymine. OTTO GERNGROSS (*Ber.*, 1905, 38, 3408—3411).—6-Chloro-2:4-dimethoxy-5-methylpyrimidine, prepared by the action of methyl alcohol and sodium methoxide on 2:4:6-trichloro-5-methylpyrimidine (preceding abstract), crystallises from light petroleum in flat needles, melts at $76-77^{\circ}$, and when reduced with zinc dust and alcohol gives 2:4-dimethoxy-5-methylpyrimidine. This crystallises from light petroleum in flat needles, melts at 60° , and boils at 322° under 758 mm. pressure; the *platinichloride* melts and decomposes at 185° . On heating the base with concentrated hydrochloric acid on the water-bath, thymine (2:4-dihydroxy-5-methylpyrimidine) is obtained identical with the natural base.
W. A. D.

Condensation Products of Alloxan with Saturated Ketones. OTTO KÜHLING (*Ber.*, 1905, **38**, 3003—3007).—Alloxan condenses with acetophenone, ethoxyacetophenone, and dibenzyl ketone, in the presence of hydrogen chloride, in aqueous-alcoholic solution cooled by ice.

Phenacyldialuric acid, $\text{COPh}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\left\langle\begin{smallmatrix}\text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\right\rangle\text{CO}, \text{H}_2\text{O}$, formed from alloxan and acetophenone, crystallises from boiling water in small, white needles, melts and decomposes at 212° , and is moderately soluble in hot water, alcohol, acetone, or glacial acetic acid. It forms an amorphous, white precipitate with silver nitrate in neutral solution, reacts with bromine in warm glacial acetic acid solution, forming a substance which crystallises in white needles and melts at 214° , and when shaken with benzoyl chloride in dilute sodium hydroxide solution yields *phenacylalanturnic acid*, $\text{COPh}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH}\end{smallmatrix}\right\rangle$, which crystallises from water in white needles and melts and decomposes at 159° . The *acetyl* derivative, $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2$, formed by boiling phenacyldialuric acid with acetic anhydride, separates from aqueous acetone in white crystals, melts and decomposes at $226\text{--}227^\circ$, and is soluble in aqueous sodium carbonate.

p-Ethoxyphenacyldialuric acid, $\text{C}_{14}\text{H}_{14}\text{O}_6\text{N}_2$, formed from *p*-ethoxyacetophenone and alloxan, crystallises in small, white leaflets, melts and decomposes at 214° , and is easily soluble in acetone.

α -Diphenylacetonyldialuric acid,



from dibenzyl ketone and alloxan, separates from boiling alcohol in white, crystalline aggregates, melts and decomposes at 233° , and is sparingly soluble in water or acetone. G. Y.

Quinazoline. III. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1905, **38**, 3559—3562. Compare *Abstr.*, 1903, i, 445; 1904, i, 1060; Gabriel and Stelzner, *Abstr.*, 1896, i, 506).—Dihydroquinazoline is obtained in a yield of 25 per cent. of the theoretical by boiling 4-chloroquinazoline with hydrogen iodide in glacial acetic acid solution, adding water, and treating the periodide so formed with sulphur dioxide in aqueous solution. When boiled with phosphorus oxychloride and poured on to ice, 4-hydroxy-6-methylquinazoline, melting at 255° (m. p. 251° ; Ehrlich, *Abstr.*, 1902, i, 25), and 4-oxy-8-methylquinazoline (Findelee, *Ber.*, 1905, **38**, 3555) yield 4-chloro-6-methylquinazoline, $\text{C}_6\text{H}_3\text{Me}\left\langle\begin{smallmatrix}\text{N}=\text{CH} \\ \text{CCl}:\text{N}\end{smallmatrix}\right\rangle$, melting at $107\text{--}108^\circ$, and 4-chloro-8-methylquinazoline, melting at 130° , respectively. These crystallise from light petroleum in needles, and when treated with fuming hydriodic acid are reconverted into the oxy-compounds.

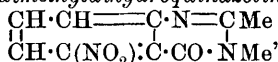
Potassium *o*-carbamidobenzoate, formed when an aqueous solution of anthranilic acid and potassium cyanate is evaporated to dryness on the water-bath, is converted into 2:4-dioxyquinazoline when evaporated with hydrochloric acid. 2:4-Dichloroquinazoline is formed when the dioxy-compound is boiled with phosphorus pentachloride and

oxychloride in a reflux apparatus. It is reduced by fuming hydriodic acid and phosphonium iodide at 50—60° with formation of 4-hydroxyquinazoline, but when treated with hydrogen iodide in glacial acetic acid it yields dihydroquinazoline in a yield of 43 per cent. of the theoretical. G. Y.

Synthesis of 5-Nitro-4-keto-2-methyldihydroquinazolines from 6-Nitroacetylanthranil and Primary Amines. MARSTON T. BOGERT and HARVEY AMBROSE SEIL (*J. Amer. Chem. Soc.*, 1905, **27**, 1305—1310).—Bogert and Chambers (this vol., i, 612) have shown that 6-nitroacetylanthranil readily condenses with primary amines to form quinazolines. The quinazolines obtained with methylamine, ethylamine, *n*- and isopropylamines, *iso*- and *sec*-butylamines, *iso*amylamine, and allylamine are now described. These compounds are white, crystalline solids, sparingly soluble or insoluble in water, carbon tetrachloride, carbon disulphide, light petroleum, cold benzene, or cold ether, moderately soluble in the two last-mentioned solvents at the boiling point and in cold methyl, ethyl, or amyl alcohol or acetone, but easily soluble in chloroform, ethyl acetate, hot alcohol, or hot acetone.

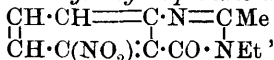
5-Nitro-4-keto-2-methyldihydroquinazoline, obtained by Bogert and Chambers (*loc. cit.*) from 6-nitroacetylanthranil and ammonia, is freely soluble in alkalis, moderately so in water, and in these respects differs from the quinazolines now described. 6-Nitroacetylanthranilamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NHAc}) \cdot \text{CO} \cdot \text{NH}_2$, formed as an intermediate product in this condensation, is a white, crystalline substance which melts at 218—219° (corr.), is soluble in dilute alkali, and when heated in alkaline solution is converted into the quinazoline.

5-Nitro-4-keto-2 : 3-dimethyldihydroquinazoline,



from 6-nitroacetylanthranil and methylamine, melts at 203° (corr.).

5-Nitro-4-keto-2-methyl-3-ethyldihydroquinazoline,



from 6-nitroacetylanthranil and ethylamine, melts at 208° (corr.).

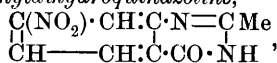
5-Nitro-4-keto-2-methyl-3-*n*-propyldihydroquinazoline and the corresponding isopropyl derivative melt at 204—205° (corr.) and 219—220° (corr.) respectively. 5-Nitro-4-keto-2-methyl-3-isobutyldihydroquinazoline and the corresponding *sec*-butyl derivative melt at 202—203° (corr.) and 209—210° (corr.) respectively. 5-Nitro-4-keto-2-methyl-3-isoamyldihydroquinazoline melts at 213—214° (corr.). 5-Nitro-4-keto-2-methyl-3-allyldihydroquinazoline is dimorphous, crystallising in rhombic plates or long needles, and melts at 160—161° (corr.).

A comparison has been made of various methods of preparing 6-nitroacetylanthranil, and the results are recorded. E. G.

Synthesis of 7-Nitro-4-keto-2-alkyldihydroquinazolines from 4-Nitroacetylanthranilic Acid and from 4-Nitroacetylanthranil. MARSTON T. BOGERT and S. H. STEINER (*J. Amer. Chem. Soc.*, 1905, **27**, 1327—1331).—The methods of preparation of 4-nitro-2-

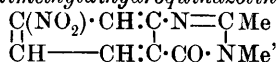
acetylaminobenzoic acid (Wheeler and Barnes, Abstr., 1898, i, 368) are compared. When this acid is boiled for 5—10 minutes with excess of acetic anhydride, 4-nitroacetylanthranil, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CO} \\ \diagup \\ \text{N} \end{smallmatrix} \text{Ac}$, is produced, which crystallises in pale green cubes, melts at $137\text{--}138^\circ$ (corr.), is readily hydrolysed by moisture, and condenses with primary amines to form substituted anthranilamides and quinazolines. 4-Nitro-2-acetylaminobenzamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NHAc}) \cdot \text{CO} \cdot \text{NH}_2$, obtained by the action of ammonia on 4-nitroacetylanthranil, crystallises in pale yellow needles, is easily soluble in hot alcohol, fairly so in ammonia, and sparingly so in acetic acid; when heated, it melts at $218\text{--}223^\circ$ (corr.) and becomes converted into the quinazoline.

7-Nitro-4-keto-2-methylidihydroquinazoline,



obtained by heating ammonium 4-nitroacetylanthranilate at 225° , or by the action of ammonia on 4-nitroacetylanthranil, crystallises in long, pale green needles, melts at $275\text{--}277^\circ$ (corr.), and is soluble in hot water, hot alcohol, or alkalis, and slightly so in acetic acid or hot ethyl acetate; the hydrochloride forms silky, greenish-white needles.

7-Nitro-4-keto-2 : 3-dimethylidihydroquinazoline,



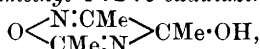
obtained by warming 4-nitroacetylanthranil with an aqueous solution of methylamine, forms light yellowish-green crystals, melts at $144\text{--}145^\circ$ (corr.), and is soluble in alcohol. E. G.

Compounds of Azines of the Anthraquinone Series [with Formaldehyde]. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 159942).—The azines of the anthraquinone series (this vol., i, 720, 797) combine with formaldehyde in concentrated sulphuric acid solution below 50° . The new products, the constitution of which is unknown, are blue dyes more readily soluble and of greener shade than the parent substances. They dissolve in hot aniline or pyridine to bluish-green solutions, and in concentrated sulphuric acid to olive-brown solutions.

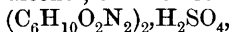
C. H. D.

Condensation of isoNitrosoketones with Aldoximes. Formation of Oxadiazines. I. OTTO DIELS and RUDOLF VAN DER LEEDEN (*Ber.*, 1905, 38, 3357—3371).—When diacetylmoxime is heated with either anhydrous or aqueous hydrogen chloride, the products are the dioxime and a compound, $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2 \cdot \text{HCl}$. The base, $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$, may be obtained by the direct condensation of diacetylmoxime with acetaldoxime at $50\text{--}60^\circ$, and the reaction appears to be characteristic of aldoximes, since benzaldoxime yields a similar base, $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2$. The mode of formation and general properties harmonise best with the constitutional formula, $\text{O} \begin{smallmatrix} \text{N} : \text{CMe} \\ \diagup \quad \diagdown \\ \text{CR} : \text{N} \end{smallmatrix} \text{CMe} \cdot \text{OH}$.

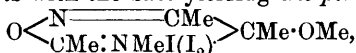
4-Hydroxy-3 : 4 : 6-trimethyl-1 : 2 : 5-oxadiazine,



crystallises from hot water in flat needles, melts and decomposes at 203° . Ten c.c. of the hot saturated solution contain 1.7 grams of base. The solution is neutral, gives a red coloration with ferric chloride, and reduces silver and platinum salts on heating, but not Fehling's solution. It dissolves readily in dilute acids, and concentrated nitric acid decomposes it yielding diacetyl; it dissolves in concentrated sulphuric acid, but is not decomposed by this reagent even at 150° . The *hydrochloride* crystallises from acetone in long prisms melting at 131° , and readily soluble in water, alcohol, or chloroform. The *sulphate*,

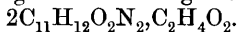


crystallises from alcohol in prisms and melts at 168° . The *sodium salt*, $\text{C}_6\text{H}_9\text{O}_2\text{N}_2\text{Na}, 4\frac{1}{2}\text{H}_2\text{O}$, crystallises from hot alcohol in needles. Methyl iodide reacts with the base yielding the *periodide*,



which crystallises from methyl alcohol in deep reddish-brown needles melting at 112° after sintering at $108-110^{\circ}$.

4-*Hydroxy-6-phenyl-3:4-dimethyl-1:2:5-oxadiazine*, obtained by the action of benzaldehyde on a mixture of hydroxylamine hydrochloride and diacetylmonoxime, crystallises from methyl alcohol, becomes brown at 210° , and melts and decomposes at 220° . It dissolves sparingly in most organic solvents with the exception of acetic acid, from which it crystallises in glistening needles having the composition

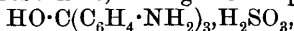


When oxidised with nitric acid, the base yields benzoic acid, and when decomposed by hydrochloric acid at 180° , benzaldehyde. The *hydrochloride* crystallises from hot acetone in colourless needles melting at 146° .

With methyl iodide, it yields a mixture of products, from which the *periodide*, $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}_3\text{I}_3$, has been isolated; this crystallises from methyl alcohol in dark reddish-brown needles melting at 126° . J. J. S.

Action of Sulphurous Acid on the Triphenylmethane Dyes.

KARL DÜRRSCHNABEL and HUGO WEIL (*Ber.*, 1906, **38**, 3492—3493).—An *acid sulphite* of *p*-rosaniline, having the composition



is obtained in pale red crystals by suspending rosaniline in water, passing in sulphur dioxide until the dye dissolves to an orange-yellow solution, driving off the excess of sulphur dioxide by heating until the red colour reappears, and allowing the solution to cool; the salt is sparingly soluble in water, and on heating at 90° loses water and passes from the carbinol into the quinonoid salt.

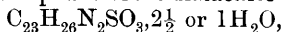
The *normal sulphite*, $(\text{C}_{19}\text{H}_{17}\text{N}_3)_2, \text{H}_2\text{SO}_3$, of *p*-rosaniline was obtained by suspending the preceding compound in water and heating until the solution became red and metallic crystals with a green lustre were produced. The salt is very stable, is not altered by heating at 160° , and is not decomposed by prolonged heating with sodium carbonate solution; sodium hydroxide, however, converts it into rosaniline.

Triaminotriphenylcarbinol-leucosulphonic acid, $\text{C}_{19}\text{H}_{19}\text{N}_3\text{SO}_3, 3\frac{1}{2}\text{H}_2\text{O}$, separates slowly from a saturated solution of *p*-rosaniline in sulphurous acid and forms yellow, minute crystals which slowly lose a part of

their water of crystallisation. Unlike the acid sulphite, this compound can be momentarily dissolved in very dilute sodium carbonate solution, but soon deposits the normal sulphite.

A solution of crystal-violet in sulphurous acid deposits a *compound*, $C_{25}H_{31}N_3SO_3 \cdot 2\frac{1}{2}H_2O$, in pale violet crystals which slowly lose water of crystallisation and pass into the intensely coloured quinonoid salt.

The corresponding compound from malachite-green,



forms in the fresh state, pale green crystals which soon develop an intense green colour.

T. M. L.

Salts of the Crystal-violet Group. JULIUS SAND (*Ber.*, 1905, 38, 3642—3654. Compare Hantzsch, *Abstr.*, 1900, i, 365).—A mixture of a solution of crystal-violet and hydrochloric acid, when kept at a constant temperature, shows a diminution of electrical conductivity as the time increases until a limiting minimum is reached. This phenomenon indicates a diminution of hydrogen ions due to the formation of a polyacid salt, and ultimately a state of equilibrium between the mono-salt, hydrochloric acid, and the polyacid salt (called by the authors trisalt- β) is attained. This trisalt- β does not appear to be analogous to Hantzsch's trisalt, $C(C_6H_4NMe_2)_3Br(HBr)_2$, which is termed trisalt- α .

The constant K for $(\text{mono-salt})(HCl)^2/(\text{trisalt-}\beta)$ is 1.12×10^{-3} .

Hantzsch's trisalt- α on solution in water gives immediately a constant conductivity which is practically identical with the additive value calculated for 1 equivalent of mono-salt + 2 of hydrobromic acid. The conversion into mono-salt is thus practically instantaneous and the constant K for this change can thus not be calculated.

The constants for the incomplete changes: (1) mono-salt + $2HCl \rightarrow$ trisalt- β K_1 , (2) trisalt- $\beta \rightarrow$ mono-salt + $2HCl$ K_2 , have been found to be $K_1 = 5.2$ and $K_2 = 5.8.10^{-3}$.

The decomposition constant, K_2 , for the trisalt- β is not the same as the constant for Hantzsch's carbinol trisalt, ($K_3 = 2 \times 10^{-2}$), and hence the two salts cannot be identical. Full details of the calculations are given.

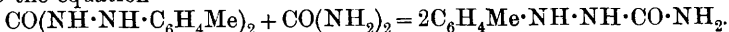
J. J. S.

Action of Hydroxylamine on *aposafranones*. OTTO FISCHER and EDUARD HEPP (*Ber.*, 1905, 38, 3435—3438. Compare *Abstr.*, 1903, i, 654; Kehrman and de Gottrau, this vol., i, 670).—In agreement with Kehrman and de Gottrau it is found that the compounds obtained by the action of hydroxylamine on *aposafranone*, *isorosindone*, and *ethylisorosindone* are not oximes but the isomeric amino*aposafranones*. Hydroxylamine salts react with *aposafranone*, whereas ammonium chloride is without any influence.

Amino*aposafranone*, prepared by heating *aposafranone* with concentrated alcoholic ammonia under pressure at 140° , is identical with that previously prepared by means of hydroxylamine; both compounds, when heated with sulphuric acid, give the same hydroxy*aposafranone*, proving the amino-group to occupy the ortho-position to the oxygen.

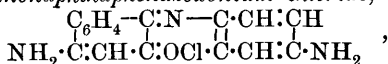
E. F. A.

Preparation of *m*-Tolylsemicarbazide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 160471. Compare this vol., i, 383).—In place of *m*-tolylhydrazine, di-*m*-tolylcarbazide may be allowed to react with carbamide at 160°, yielding *m*-tolylsemicarbazide according to the equation



The same compound is obtained when di-*m*-tolylsemicarbazide is heated with ammonia at 180°. C. H. D.

Azoxonium Compounds. III. FRIEDRICH KEHRMANN (*Ber.*, 1905, 38, 3604—3607. Compare Abstr., 1901, i, 484; this vol., i, 930).—4 : 8-Diaminonaphthaphenazoxonium chloride,



is formed by boiling 2 : 5-diaminophenol hydrochloride with 4-amino-1 : 2-naphthaquinone in alcoholic solution in a reflux apparatus and treating the reaction-product with hydrochloric acid. It crystallises from alcohol in slender, metallic green needles containing water, which is lost at 130°, and is readily soluble in hot water, forming a violet solution with dark red fluorescence, or in alcohol, forming a blue solution with strong red fluorescence; the reddish-brown solution in concentrated sulphuric acid becomes yellow on addition of a small quantity of water, or violet on addition of much water and partial neutralisation of the acid. The aqueous solution dyes tannin-mordanted cotton a bluish-violet, which is fast to soaping and moderately so to light. G. Y.

endoIminotriazoles. FIRMA EMANUEL MERCK (D.R.-P. 159692).—Triarylated aminoguanidines condense with carboxylic acids or their chlorides to form endoiminotriazoles. Thus, triphenylaminoguanidine and concentrated formic acid react at 170—175° to form endoanilino-

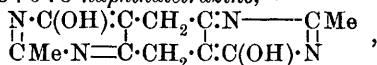
NPh—N
diphenyltriazole, $\begin{array}{c} | \\ \text{CH} < \text{NPh} \\ | \\ \text{NPh} \end{array} \parallel \text{C}$, which crystallises from alcohol in

glistening, yellow leaflets, or from chloroform and light petroleum in needles. The salts are highly crystalline, the *nitrate* being insoluble and the *sulphate* and *tartrate* very soluble in water.

endoAnilinotriphenyltriazole, from benzoyl chloride and triphenylaminoguanidine, separates from alcohol in glistening, intensely yellow needles and melts at 231—232°. The sparingly soluble *nitrate* melts at 284°; the *hydrochloride* forms flat, colourless needles, melts at 296°, and dissolves readily in water. endoAnilinodi-*p*-tolyltriazole separates from chloroform and light petroleum in yellow needles and melts at 167°. C. H. D.

Condensation of Ethyl Succinylsuccinate with Acetamidine. 4 : 9-Dihydroxy-2 : 7-dimethyl-5 : 10-dihydro-1 : 3 : 6 : 8-naphthate-tetrazine. MARSTON T. BOGERT and ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1905, 27, 1302—1305).—It has been shown (this vol., i, 841) that ethyl succinylsuccinate condenses with gua- ni-

dine to form a naphthatetrazine. A similar condensation takes place with acetamidine with production of 4 : 9-dihydroxy-2 : 7-dimethyl-5 : 10-dihydro-1 : 3 : 6 : 8-naphthatetrazine, .



which is obtained as a white powder, and dissolves in ammonia forming a solution with a blue fluorescence, but is insoluble in the usual organic solvents ; when heated, it does not melt, but becomes charred. The *sodium* derivative crystallises with $6\text{H}_2\text{O}$. E. G.

Nitrophenyldiguanides. RICHARD HERMANN (*Monatsh.*, 1905, 26, 1021—1037).—Nitroanilines do not interact with dicyanodiamide.

p-Nitrophenyldiguanide is obtained in the form of its *sulphate*, $(\text{C}_8\text{H}_{10}\text{O}_2\text{N}_6)_2, \text{H}_2\text{SO}_4$, by treating phenyldiguanide hydrochloride with nitric acid of sp. gr. 1.51 and concentrated sulphuric acid at 30—40°. The sulphate crystallises in matted, white, hair-like needles and melts at about 254°. The free base, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_6, \text{H}_2\text{O}$, separates from alcohol in yellow doubly refractive, prismatic leaflets, loses H_2O at 105°, and melts at 182°. The *picrate* forms a yellow, amorphous precipitate ; the *silver nitrate* derivative is obtained as a yellow, flocculent precipitate. When heated with concentrated aqueous potassium hydroxide at 125—130°, the base yields *p*-nitroaniline.

op-Dinitrophenyldiguanide, $\text{C}_8\text{H}_9\text{O}_4\text{N}_7$, formed by the action of nitric acid of sp. gr. 1.51 and concentrated sulphuric acid on *p*-nitrophenyldiguanide at 75—80°, is obtained in the form of its *sulphate*, $(\text{C}_8\text{H}_9\text{O}_4\text{N}_7)_2, \text{H}_2\text{SO}_4$, which crystallises in yellow needles and melts at 234°. The free base crystallises in doubly refractive, orange-yellow needles, melts at 193°, has a slight basic reaction towards litmus, and yields a yellow, amorphous *precipitate* with silver nitrate. The *oxalate* crystallises in nodular aggregates of broad needles ; the *picrate* forms a yellow precipitate. When heated with dilute sulphuric acid at 160—170°, the base is hydrolysed with formation of 2 : 4-dinitroaniline which melts at 181—182° (m. p. 175° ; Rudnew, this Journal, 1871, 24, 712).

2 : 4 : 6-Trinitrophenyldiguanide *sulphate*, $(\text{C}_8\text{H}_8\text{O}_6\text{N}_8)_2, \text{H}_2\text{SO}_4$, formed by the action of nitric acid of sp. gr. 1.51 and concentrated sulphuric acid on *op*-dinitrophenyldiguanide at 105—110°, crystallises in microscopic, broad, yellow leaflets, melts at 270°, and is hydrolytically dissociated when boiled with water or alcohol. The free base, $\text{C}_8\text{H}_8\text{O}_6\text{N}_8$, crystallises in doubly refractive, microscopic, short leaflets, which appear golden by transmitted, reddish-violet by reflected light, melts at about 239°, and is extremely hygroscopic. When hydrolysed with dilute sulphuric acid, the base yields 2 : 4 : 6-trinitroaniline.

p-Aminophenyldiguanide *sulphate*, $(\text{C}_8\text{H}_{12}\text{N}_6)_2, \text{H}_2\text{SO}_4$, is formed by electrolytic reduction of *p*-nitrophenyldiguanide in concentrated sulphuric acid and alcohol, with a current density of 3—3.5 amperes and an *E.M.F.* of 1 volt. ; it crystallises in broad, white needles and prismatic leaflets, forms with copper sulphate and aqueous alkali hydroxide a rose-red *copper* derivative consisting of fan-shaped aggregates of slender needles, with auric chloride forms a colloidal gold solution, and reduces

ammoniacal silver solutions. When heated with dilute sulphuric acid at 170° , it is hydrolysed with formation of *p*-phenylenediamine.

G. Y.

A New Method of Formation of Diazo-compounds and a General Method for Determining the Constitution of Azo-dyes. OTTO SCHMIDT (*Ber.*, 1905, **38**, 3201—3210).—The action of fuming nitric acid, cooled by ice, on azo-dyes containing an auxochromic amino- or hydroxyl group in the para-position to the azo-group leads to the formation of the diazo-compound from which the dye is prepared, the other component appearing as a nitro-derivative; if the auxochromic group is in the ortho-position, the decomposition takes place completely only with β -naphthol dyes, but partially with *p*-cresol dyes, whilst the reaction takes place only to a small extent or does not take place with azo-dyes containing the auxochromic group in the meta-position. Other azo-compounds, such as azobenzene, are not decomposed by fuming nitric acid.

Azoxy-compounds which contain a *p*-amino-group, such as *pp'*-tetraethyldiaminoazoxybenzene, are decomposed by fuming nitric acid with formation of diazo-compounds. These azoxy-compounds, as also azo-dyes containing an auxochromic group in the para-position, are decomposed in the same manner by chromic or permanganic acids in glacial acetic acid solution.

Helianthin (16.4 grams) yields 8.1 grams of *op*-dinitrodimethylaniline, 1.2 grams of tetranitrodimethylaniline, and diazobenzene-sulphonic acid which, when coupled with β -naphthol, forms 19.2 grams of the dye, $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, which crystallises in glistening, bronze leaflets. *Tetranitrodimethylaniline*, $\text{C}_7\text{H}_5\text{O}_8\text{N}_5$, crystallises from alcohol, is yellow, and melts at 128 — 129° .

p-Nitro-*p'*-methoxyazobenzene, $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}_3$, is formed by the action of methyl iodide and sodium methoxide on *p*-nitro-*p'*-hydroxyazobenzene in boiling methyl-alcoholic solution. It crystallises in yellowish-red, flat needles, melts at 157.5 — 158° , and when 5 grams are treated with cooled fuming nitric acid yields 2.5 grams of *op*-dinitroanisole melting at 88° , and the diazo-compound, which, with β -naphthol, forms 4.41 grams of *p*-nitrobenzeneazo- β -naphthol, melting at 251.2 — 252.5° .

When treated with fuming nitric acid, 4 grams of orange II yield 1.7 grams of a nitro-derivative of β -naphthol and diazotised sulphanilic acid, which, when coupled with phenol, forms 2 grams of the azo-dye. In the same manner, 2 grams of β -naphtholazobenzene-*o*-carboxylic acid yield 1.4 grams of a nitro- β -naphthol, and 1.8 grams of the dye is recovered by coupling the diazo-compound formed with β -naphthol.

Satisfactory yields of diazo-compounds are obtained from *p*-ethoxy-*p'*-hydroxyazobenzene, *p*-hydroxyazobenzenesulphonic acid, benzene-azo- β -naphthol, and *p*-ethoxybenzeneazo- β -naphthol; but *m*-hydroxyazobenzene, the product obtained on coupling diazotised anthranilic acid with *p*-cresol, azobenzene, *p*-azotoluene, and tetramethyl-*mm'*-diaminoazobenzene, do not yield, or yield only small amounts of, diazo-compounds. [Compare Meldola and Morgan, *Trans.*, 1899, **55**, 608; Meldola and Hanes, *ibid.*, 1894, **65**, 841.]

G. Y.

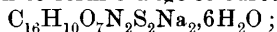
Stability of Diazotised *p*-Nitroaniline. CARL SCHWALBE (*Zeit. Farb. Text. Ind.*, 1905, 4, (xviii), 433—456).—The influence of the amount of free hydrochloric acid, free nitrous acid, sodium acetate, or salt on the keeping power of diazotised *p*-nitroaniline has been investigated. The diazo-solutions used were prepared from purified commercial nitrosoamine-red and were titrated against β -naphthol both at the beginning of each experiment and 24 hours later. The experiments show the very harmful influence on the keeping-power exercised by small quantities of nitrous acid, which is still more marked in presence of sodium acetate. Mineral salts are beneficial in increasing the stability when used in conjunction with sodium acetate. Excess of hydrochloric acid also acts beneficially on the keeping-power.

E. F. A.

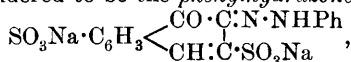
Properties of *p*-Azophenetole. FRIEDRICH DREYER and TH. ROTARSKI (*Chem. Centr.*, 1905, ii, 1016—1017; from *Isvert. Petersburg. Polytechn. Inst.*, 1905, 135—157).—*p*-Azophenetole, prepared by the reduction of *p*-nitrophenetole with sodium ethoxide, is dimorphous and crystallises from alcohol; it melts and solidifies at 159.35°. The transformation point of the α - into the β -modification is 93.65°. The solubility of the compound in glacial acetic acid is 0.153 gram-molecules per litre at 89.2°, 0.176 at 91°, 0.185 at 93°, 0.209 at 95.6°, 0.232 at 97.2°, and 0.252 at 99.6°; the solubility curve shows a point of inflection at 94.7° corresponding with the temperature of transformation. The α -form crystallises in rhombic plates, has a sp. gr. 1.2314 at 21°/4°, a specific heat 0.350 between 93.7° and 20°, and a coefficient of expansion 0.00033 from 30° to 93.7°, and 0.00078 from 93.7° to 158°. The β -form has a sp. gr. 1.1977 at 21°/4° and a specific heat 0.502 from 93.7° to 159.3°. The molten compound is not doubly refractive and has a specific heat 0.521 from 161.1° to 175.5°. The heat developed by the change of the β - into the α -form is 1.6 and the latent heat of fusion 35.0 calories.

E. W. W.

Constitution of the Hydroxyazo-compounds. HERBERT TEICHNER (*Ber.*, 1905, 38, 3377—3380).—Sodium 1:2-naphthaquinone-3:6-disulphonate combines with phenylhydrazine sulphate in cold dilute alcoholic solution to form orange-coloured needles,

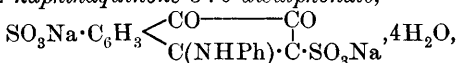


the product is considered to be the *phenylhydrazone*,



of the original substance. It is not a derivative of 2-hydroxy-1:4-naphthaquinone, as it does not possess tinctorial properties, and, moreover, it is reducible by an excess of phenylhydrazine to 1:2-dihydroxy-naphthalene-3:6-disulphonic acid. It does not condense, moreover, like an ortho-diketone with *o*-tolylenediamine.

The following substances were prepared for comparison. *Sodium 4-anilino-1:2-naphthaquinone-3:6-disulphonate*,



is obtained by the action of aniline on sodium 1:2-naphthaquinone-

3:6-disulphonate; it forms orange-coloured crystals and condenses with *o*-tolylenediamine, giving a bluish-red, crystalline product, $C_{23}H_{15}O_6N_3S_2Na_2$. Aniline gives with sodium 1:2-naphthaquinone-6-sulphonate a product which separates in dark red crystals.

W. A. D.

Aminoazo-dyes from Chlorochromotropic Acid. FARBERWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 160281).—Hypochlorous acid and its salts react with chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid) yielding a *chlorochromotropic acid*, in which the chlorine atom probably occupies the ortho-position to one of the hydroxyl groups. This acid does not readily combine with diazotised amines, but combines with diazotised nitroamines, and the resulting compounds may be reduced with sodium sulphide at 50—60° to blue aminoazo-dyes. Thus *p*-nitroaniline, chloro-*p*-nitroaniline, or 2:5-nitroaminoquinol dimethyl ether may be employed. C. H. D.

A New Method of Formation of Osotetrazones. WALTER DIECKMANN and LUDWIG PLATZ (*Ber.*, 1905, 38, 2986—2990. Compare von Pechmann, *Abstr.*, 1898, i, 62).—*α*-Chloroglyoxalphenylhydrazone, $COH \cdot CCl \cdot N \cdot NPh$, is formed by the action of phenyldiazonium chloride on chloromalonaldehyde in aqueous sodium acetate solution cooled by ice; it crystallises from alcohol or benzene in long, yellow needles, melts at 141°, is readily soluble in warm alcohol, ether, glacial acetic acid, benzene, chloroform, light petroleum, or cold acetone, and dissolves in concentrated sulphuric acid, forming a green solution, which becomes red, changing to a dirty-green with ferric chloride, or bluish-violet with potassium dichromate; when treated with aqueous alkali hydroxides, it decomposes and yields a strong isonitrile odour.

Chloroglyoxalosazone, $NHPh \cdot N \cdot CH \cdot CCl \cdot N \cdot NHPh$, formed by the action of phenylhydrazine on *α*-chloroglyoxalphenylhydrazine in alcoholic solution, crystallises in yellow leaflets, melts at 142·5°, is less soluble than the hydrazone, and dissolves in concentrated sulphuric acid, forming a yellow solution which becomes green, changing to blue on addition of potassium dichromate. When treated with alcoholic potassium hydroxide, the osazone is converted into glyoxalosotetrazone, which melts at 152°.

α-Chloro-*β*-methylglyoxal-*α*-phenylhydrazone, $COMe \cdot CCl \cdot N \cdot NHPh$, formed by the action of phenyldiazonium chloride on *α*-chloroacetylacetone in presence of potassium acetate in aqueous-alcoholic solution, crystallises in yellow needles and melts at 136·5°; it is moderately soluble in warm alcohol, ether, benzene, chloroform, glacial acetic acid, or cold acetone, and when treated with aqueous alkali hydroxide gives an isonitrile odour. It interacts with phenylhydrazine to form *α*-chloro-*β*-methylglyoxalosazone, $NHPh \cdot N \cdot CMe \cdot CCl \cdot N \cdot NHPh$, which crystallises from glacial acetic acid in lemon-yellow leaflets, melts and decomposes at 182·5°, and dissolves in concentrated sulphuric acid to form a yellow solution which becomes bluish-violet on addition of potassium dichromate. When treated with alcoholic

potassium hydroxide, the osazone forms methylglyoxalosotetrazone, melting at 106—107° and decomposing at 124°. G. Y.

The Bence-Jones Proteid. EMIL ABDERHALDEN and OTTO ROSTOCKI (*Zeit. physiol. Chem.*, 1905, 46, 125—135).—The proteid was obtained from the urine in a case of bone sarcoma. On heating, it is precipitated at 50—60°; this precipitate dissolves on boiling, and reappears on cooling; other properties which are described show it to be similar to the proteid described in previous cases. When a solution of it is injected into rabbits, it does not pass into the urine, and a precipitin is formed in the rabbits' blood, which, however, acts not only on the Bence-Jones proteid, but also on the proteids of normal serum. On hydrolysis, 100 grams yield—glycine, 1.7; alanine, 4.5; leucine, 10.6; proline, 1.9; phenylalanine, 1.5; glutamic acid, 6.0; aspartic acid, 4.5; and tyrosine, 1.7 grams. Lysine, arginine, and histidine were also detected. W. D. H.

The Composition of the Proteid of *Aspergillus Niger*. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1905, 46, 179—186).—*Aspergillus niger* was cultivated on various nitrogenous media; its proteid matter yields on hydrolysis, glycine, alanine, leucine, glutamic and aspartic acids. Aromatic products such as tyrosine and phenylalanine were not discovered. The experiments point to the independence of the proteid and the medium on which the mould is grown, but this cannot be asserted with confidence until quantitative experiments are made. W. D. H.

Influence of Acids and Alkalis on the Swelling of Gelatin. WOLFGANG OSTWALD (*Pflüger's Archiv*, 1905, 108, 563—589).—The swelling of gelatin in acids and alkalis depends, in a complex manner, on the concentration, the rate increasing with concentration to a maximum at $N/40$ for hydrochloric acid and $N/36$ for potassium hydroxide. With higher concentrations, the rate again diminishes, the fall being at first rapid, then very gradual. Similar results are obtained with other acids and alkalis. The type of curve obtained shows a general parallelism with those representing other properties. The author points out that any theory which attempts to explain the physico-chemical properties of colloids must account for these peculiar curve relations.

The absolute value of the swelling is much larger than in pure water; the absorption of liquid being with acid 3—4 times, and with the optimum alkali 3 times as much. J. J. S.

Formation of Complex Proteids from Peptones. LEOPOLD SPIEGEL (*Ber.*, 1905, 38, 2696—2702. Compare Henninger, Abstr. 1878, 802, 989; Hofmeister, Abstr., 1879, 950; Loew, Abstr., 1888, 358; Schroetter, Abstr., 1896, i, 515; Blum, Abstr., 1896, i, 658; Lawroff and Salaskin, Abstr., 1903, i, 136; Nürnberg, Abstr., 1904, ii, 187).—When a 5 per cent. solution of commercial peptone is acidified slightly with acetic acid and 1 part of aldehyde in 40 per cent. solution added for each part of peptone, there is formed immediately a

flocculent precipitate which coagulates to a leathery mass; when warmed with dilute sodium hydroxide, this partially dissolves to form a solution which on acidification with acetic acid and warming deposits a small coagulate on the walls of the glass vessel.

The precipitate obtained from a peptone of unknown genesis contained C=48.78, H=7.39, N=16.63, S=1.29, and ash=0.023 per cent., whilst that from a specimen of Witte's peptone contained C=49.55, 50.31, H=8.63, 7.55, N=13.75, S=1.11, and ash=0.165 per cent. The filtrate from the flocculent precipitate becomes opaque on warming, and this precipitation is greatly increased on adding acetic acid, whereas a solution of peptone slightly acidified with acetic acid remains clear when heated by itself, or with a further addition of acetic acid, or in presence of 1 per cent. of sodium chloride. The filtrate gives positive results with the xanthoprotein, Spiegler's, the biuret, and Adamkiewicz's reactions for albumin, as also with concentrated nitric and sulphuric acids, and with concentrated sulphuric acid and saccharose; it blackens alkaline lead solutions on boiling. An acidified solution of peptone gives a yellowish-brown coloration with the xanthoprotein and only a slow precipitation with Spiegler's reagent.

Fractional precipitation experiments according to Pick's method (Abstr., 1898, i, 288) show that in the formaldehyde-peptone filtrate the albuminoses which are soluble in semi-saturated ammonium sulphate solution have been converted into albumins, which are easily salted out, and part of which correspond with Fuld and Spiro's euglobulin (Abstr., 1901, ii, 67).

Pure peptone is obtained by saturating an aqueous solution of Witte's peptone with ammonium sulphate, concentrating the filtrate, and precipitating the ammonium sulphate with alcohol. This, when treated with formaldehyde in aqueous solution at the winter temperature, remains clear even if saturated immediately with ammonium sulphate, but forms a precipitate if saturated after some days, and after two months becomes opaque when warmed with 1 per cent. of sodium chloride. If the treatment with formaldehyde is carried out at the summer temperature, condensation takes place immediately, with formation of a precipitate which dissolves in dilute sodium hydroxide to form a solution from which acids precipitate a substance with the properties of an alkali albuminate. The filtrate from the condensation precipitate forms a precipitate when half saturated, and again when completely saturated with ammonium sulphate.

When distilled, the alkaline solution of the condensation precipitate yields a distillate which has an odour resembling that of formaldehyde and precipitates a black powder from warm ammoniacal silver nitrate solution, but does not give the formaldehyde reaction with alkaline resorcinol. The residual alkaline liquid does not form a precipitate when acidified. The condensation precipitate does not yield formaldehyde when heated with acids. G. Y.

Adrenaline [Epinephrine], the Active Principle of the Suprarenal Glands. THOMAS B. ALDRICH (*J. Amer. Chem. Soc.*, 1905, 27, 1074—1091).—A résumé is given of the work on adrenaline

together with a discussion of its constitution. The author quotes analyses in support of the formula $C_9H_{13}O_3N$, which he was the first to ascribe to the compound (Abstr., 1901, ii, 564). A bibliography of the subject is appended. E. G.

Behaviour of Ferments towards Colloidal Solutions. EMIL REISS (*Beitr. chem. Physiol. Path.*, 1905, 7, 151—152. Compare Dauwe, this vol., i, 623).—When chloroform solutions of lecithin are shaken with solutions of ferments, it is found that part of the ferment is transferred to the chloroform solution. This holds good for rennin and trypsin. The catalase of milk adheres to the milk globules, but if these are separated from the plasma and covered with water or sodium chloride solution, the catalase is dissolved by these liquids, indicating that the enzyme is precipitated by the colloidal plasma, but in the absence of such colloids is readily soluble. J. J. S.

Catalase. PHILIP SHAFFER (*Amer. J. Physiol.*, 1905, 14, 299—312).—The main conclusion drawn from the experiments recorded is that the catalase action of plant and animal extracts liberates oxygen in a molecular condition. It is therefore not an oxidising enzyme, but destroys the peroxide in such a way that oxygen is not liberated in an active condition; the tissues are thus protected from injurious oxidation. W. D. H.

Is the Presence of a Catalase necessary for the Guaiacum Reaction? LEO LIEBERMANN and PAUL LIEBERMANN (*Pflüger's Archiv*, 1905, 108, 489—498. Compare *ibid.*, 1903, 104, 207).—Heating malt-extract above 80° , or shaking it with mercuric oxide and magnesia, destroys the catalase which causes the decomposition of hydrogen peroxide, but the solution still induces the guaiacum reaction, particularly if oil of turpentine is present. Hence the authors conclude that, contrary to the view held by Neumann-Wender (*Enzymologische Studien*, I, 28—35, Berlin, 1904), only one enzyme, the oxygen-carrier peroxydase, is necessary for inducing the reaction. J. J. S.

Precipitins. IVAR BANG (*Beitr. chem. Physiol. Path.*, 1905, 7, 149—150).—As regards limits of precipitation of precipitin, it is found in the same fraction as euglobulin, and after dialysis remains in the soluble portion and may be precipitated by sodium chloride. When the dialysed solution is heated, albumin coagulates at 64° and precipitin is contained in the filtrate.

Precipitins obtained by injecting ox-blood-serum into dogs do not always behave in the same manner; some give precipitates with both globulin and serum-albumin, others with globulin only. J. J. S.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Optical Reflection Constants and the Electromotive Condition of Chromium. AUGUST L. BERNOULLI (*Chem. Centr.*, 1904, ii, 1371 ; from *Physikal. Zeit.*, 5, 632—634).—An optical examination of chromium which had been rendered passive by exposure to air or by a boiling solution of *p*-benzoquinone in benzene has been made by Michéli's method (*Abstr.*, 1901, ii, 82). The results showed that the metal was coated with a superficial layer. The composition of this layer is, according to the author, $2\text{Cr}_2\text{O}_3\cdot\text{CrO}_3$. The maximum change of *E.M.F.* against an electrode of platinum in a solution of ammonium nitrate was found to be 0.35 volt. When the metal is made passive by the action of nitric acid, the alteration of *E.M.F.* is much greater and may reach 0.9 volt. Oxygen and nitric oxide are both absorbed by chromium, and the metal, which had been treated with nitric acid and thoroughly washed, was found to liberate a measurable quantity of nitric oxide when allowed to remain in water for several hours ; active chromium does not yield this gas under similar conditions.

E. W. W.

The Stereochemistry of Nitrogen. HUMPHREY O. JONES (*Brit. Assoc. Reports*, 1904, 1—24).—This report contains a review of the state of knowledge respecting the stereochemistry of nitrogen. An account

is given of the researches on trivalent nitrogen compounds, including substituted ammonias, cyclic compounds, oximes, hydrazones and semicarbazones, anils, and azo-compounds; and also of the quinquivalent nitrogen compounds and their optical activity. This is followed by a discussion of the various molecular configurations which have been proposed to account for the facts. Full references to the literature are given.

C. H. D.

Racemism. GIUSEPPE BRUNI and F. FINZI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 349—355).—The method given by Bruni (Abstr., 1900, ii, 269) for determining whether an optically inactive substance is a racemic or pseudoracemic compound or a mixture has been since applied by Adriani (Abstr., 1901, ii, 230) and by Smits (Abstr., 1903, i, 263) to certain definite cases. The authors now give more complete considerations concerning this method. Instead of the method of fusion, they use that of solidification with the thermometer immersed in the fused mass, which gives far more exact results and entirely avoids the errors indicated by Smits. The determination of the freezing temperatures of cryohydrates by means of the Beckmann apparatus requires, in general, larger quantities of substance than the fusion method, but with a suitable solvent which dissolves only small proportions of the isomerides a few decigrams are sufficient. Besides the inactive substance, only one active compound is required, and of this the cryohydric temperature is determined. The composition of the solution is found either by analysis or by extrapolation of the freezing curve. Increasing amounts of the *d*- or *l*-compound are then added to the cryohydrate solution of the inactive compound. If the isomerides form a simple conglomerate, the freezing point remains constant and the solution inactive. Where a true racemic compound exists, the freezing temperature falls to a certain point; further additions do not change it or the rotation of the supernatant solution. By weighing the dry residue and determining its rotatory power, the amounts of inactive and active substances can be arrived at and the equilibrium curves drawn. These vary in form according as the compound or the components are the more soluble. Where pseudoracemic mixed crystals are formed, every fresh addition alters both the freezing point and rotatory power, no invariant point being attained. Curves are given, according to Schreinemaker's method of representation (Abstr., 1893, ii, 260 and 512), for all the possible cases.

The compounds investigated by the authors are methyl diacetyl-tartrate and methyl diacetylracemate in ethylene bromide and *p*-xylene and ammonium hydrogen racemate and tartrate in water. With the first pair of compounds the racemic ester is the more soluble, and with the second pair the tartrate. In both cases, true racemic compounds are formed.

T. H. P.

Flame Spectra. CHARLES DE WATTEVILLE (*Phil. Trans.*, 1904, A., 204, 139—168. Compare Abstr., 1904, ii, 222).—By injecting the spray from saline solutions into the gas to be burned, Gouy discovered (in 1879) several new lines in the flame spectra belonging to the metals contained in the solutions, but emitted only in the vicinity of

the blue inner cone. The author, extending Gouy's observations, has studied photographically a large number of flame spectra, including the ultra-violet portions. The method employed for the production of the flame is, with slight modifications, the same as that devised by Gouy. Recorded lines are fully tabulated for lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, silver, copper, tin, lead, bismuth, chromium, iron, nickel, and cobalt. It is shown that there are many more lines in the spectra obtained by the author's method than is the case when the salt spray is not previously mixed with the gases which react to form the flame. As a rule, the lines which are found in the flame spectrum are those which are the strongest lines in the arc spectrum. On the other hand, none of the characteristic lines of the spark spectrum are ever seen in the flame spectrum. There is, however, a very marked resemblance between the flame spectrum and that of an oscillatory spark. This is especially the case with iron, nickel, and cobalt. J. C. P.

Chemical Effects of Light. Action of Hydrochloric Acid on Platinum and Gold. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 3, 295—299).—A *résumé* of work already published (Abstr., 1904, ii, 569). M. A. W.

Emanations and Radiations. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 3, 289—293).—A theoretical discussion of which a notice has already appeared (Abstr., 1904, ii, 602). M. A. W.

Genesis of Temporary Radioactivity. ED. SARASIN, THOMAS TOMMASINA, and F. JULES MICHELI (*Compt. rend.*, 1904, 139, 917—920).—The curves representing the rate of fall of the radioactivity induced on negatively charged metallic wires exposed to the air resemble the curves for the activity induced by exposure to radioactive substances. The rate of decay of activity is the same for silver, copper, aluminium, iron, and nickel whether the metals have been exposed to ordinary air or to air ionised by X-rays. The activity induced by the X-rays is not due to direct radiation, but to the ionisation which these produce in the air.

If the electroscope employed for the measurements is positively charged in one experiment and negatively in a second experiment, the curves representing decay are not superposable. The explanation of this seems to be that the induced activity emits two kinds of oppositely charged particles (α and β) which behave differently in the electroscopic apparatus in consequence of their different velocities. Experiments on the decay of the feeble activity induced on exposed wires, which are positively charged, confirm this supposition.

The observations lead to the view that the production of induced radioactivity consists in the absorption of an emanation which is formed when gases are ionised; this absorbed or adherent emanation gradually disappears in consequence of radiation, and a corresponding fall in activity is observed. H. M. D.

Secondary Radiation caused by the β - and γ -Rays of Radium. A. S. EVE (*Phil. Mag.*, 1904, [vi], 8, 669—685).—An electroscope screened from the glass tube containing the radium by means of a thick lead screen was exposed to the action of the secondary radiations caused by the action of the β - and γ -rays on various radiators. A large number of substances were employed as radiators, and although the secondary radiation is generally greater for substances of high density, it is not proportional to the density. It was found that the effective depth from which the secondary radiation proceeds varies for different materials; thus for paper the secondary radiation increases until a thickness of about 2 or 3 mm. is reached and then remains constant. A plate of lead placed behind the paper, however, would then cause an increase. By cutting off the primary β -rays it was found that the secondary radiations produced by γ - and β -primary rays are of the same character, and that about 85 per cent. of the secondary radiation is due to the β -rays. This was also confirmed by deflecting the β -rays by a magnetic field. The secondary rays are, however, different from those caused by the Röntgen rays, the latter having far greater penetrative power. The absorption of the radium secondary radiations was found to obey accurately the simple exponential equation $I = I_0 e^{-\mu x}$, and the radiations hence appear more homogeneous than the primary rays; the absorptive power of different materials is roughly in the order of their densities. The radiation from the surface when the primary rays passed through from the back was also investigated; the curve increases with thickness to a maximum, remains approximately constant, and then falls, and this is the type of curve deduced theoretically, namely, that corresponding with the difference between two simple exponential curves.

The secondary radiations produced by the γ -rays can be deflected by a magnetic field and it has been shown by Becquerel that the β -secondary rays are deviable, so that the β -, γ -, and Röntgen secondary radiations all consist of electrified particles. The author does not consider that there is any evidence that the γ -rays are negatively electrified, they are probably unchanged particles or are of the type of Röntgen rays (compare Paschen, *Abstr.*, 1904, ii, 461). It seems reasonable to suppose that the expulsion of the β -particles must be accompanied by pulses similar to those set up by the stoppage of the cathode particles, and that these pulses, analogous to the Röntgen rays, constitute the γ -rays.

L. M. J.

Absorption of α -Rays and the Classification of the α -Rays from Radium. W. H. BRAGG (*Phil. Mag.*, 1904, [vi], 8, 719—725).—The author seeks to explain various differences in the absorption phenomena of α - and β -rays by the hypothesis that the β -rays are liable to deflexion through collision, but the α -rays are not. Reasons for the probability of this being the case are given, based on the difference in magnitude of the α - and β -particles, and in support of the hypothesis the facts are brought forward that there is no scattered or secondary radiation in the case of the α -rays, and that a stream of α -rays is as sharply defined after passage through a screen as before. Since the α -rays lose energy solely by ionisation, they will reach a

distance proportional to the initial energy, and an ionisation chamber is unaffected if just out of range. The author has investigated the latter case to determine the curve obtained when the ionisation chamber is brought nearer. The effect expected was that when out of range of α -rays an effect due to β - and γ -rays would be obtained; when the α -rays just penetrate there would be a sudden appearance of ionisation which, for a distance equal to the depth of the chamber, should give a parabolic curve, afterwards a straight line. This effect was actually obtained, but in addition it was found that, as the radium is brought nearer to the chamber, there are two or three sudden changes of direction of the line, the final slope being about four times the initial. The author suggests the explanation that there are several changes, and at four of these an α -atom is expelled, so that there are four different streams of α -particles differing in initial energy (Rutherford, Abstr., 1904, ii, 223).
L. M. J.

Ionisation Curves of Radium. W. H. BRAGG and R. KLEEMAN (*Phil. Mag.*, 1904, [vi], 8, 726—738).—The ionisation in a shallow chamber brought closer to a source of α -rays, limited to a narrow cone, increases, yielding a straight line curve, for as the distance diminishes the curve includes α -rays from deeper and deeper strata in the radium. If, however, the layer is sufficiently thin, so that α -particles emerge from the lowest layers, the curve should yield a straight line terminated by a vertical portion representing the range of the particles from the lowest layer. The layers employed were obtained by evaporation of a few drops of a solution of radium bromide. The curves obtained approximate to the expected form for such a curve as indicated above, with the addition that there are four different sets of rays. The curve consists of a straight portion which curves almost vertically downwards at three points; the various portions of the curve are lettered *P*, *Q*, *R*, and *S*. If the dish is raised to a red heat, the portions *Q* and *R* disappear, so that these probably represent rays from the emanation and first induced activity, and as *P* subsequently decays it represents rays from the last induced activity; these last rays penetrate about twice as far and give rise to twice the ionisation. Although not established, it seems probable that *R* represents the effect of the emanation. In the curves there is noticeable a return towards the vertical axis in the lower portions of *P* and *S*, indicating apparently that the α -particle is more effective at the end of its course. The experiment recorded in the previous abstract was repeated with a spherical ionisation chamber, by which the separate lines referred to were more clearly obtained. The authors also give an explanation of Becquerel's observation that the curvature of a thin sheet of α -ray, when deflected by a magnet, was less at greater distances from the source.
L. M. J.

Chemical Composition of the Radioactive Gaseous Mixtures evolved from the Waters of Thermal Springs. Presence of Helium. CHARLES MOUREU (*Compt. rend.*, 1904, 139, 852—855. Compare Moissan, Abstr., 1903, ii, 209; Nasini, Abstr., 1904, ii, 399; Curie and Laborde, *ibid.*, ii, 461).—The author has examined the

radioactive gases obtained from thirteen thermal springs, and finds that after the nitrogen and oxygen have been absorbed by a mixture of lime and magnesium at a red heat (compare Maquenne, Abstr., 1896, ii, 299) a residue is obtained, varying in quantity from 0.50 to 2.11 per cent. of the original volume, and presenting the characteristic spectra of argon and helium.

M. A. W.

A Radioactive Gas in the Wiesbaden Thermal Springs.

FERDINAND HENRICH (*Zeit. angew. Chem.*, 1904, 17, 1757—1760).—The gas obtained from the Adler and Schützenhof springs, Wiesbaden, after being separated from carbon dioxide and hydrogen sulphide, affected a photographic plate. The radioactivity of the gas was also examined electrometrically.

The water of the springs is also radioactive, but becomes practically inactive when boiled.

A. McK.

Demonstration of *n*-Rays. H. BORDIER (*Compt. rend.*, 1904, 139, 972—974. Compare Rothé, Abstr., 1904, ii, 603, and Blondlot, *ibid.*, 604).—Drops of collodion containing calcium sulphide in suspension are deposited in two groups on a piece of paper; after drying and keeping in the dark for 12 hours, the sulphide is made phosphorescent by exposure to daylight for a few minutes and the paper placed face downward on a photographic plate, a source of *n*-rays in the shape of a file of tempered steel or steel shot being placed over one group of spots and a piece of lead of similar size and shape over the other group. On developing the plate after 24 hours' exposure, each spot is represented on the negative by a very black spot surrounded by a penumbra, but the penumbra which surround the spots corresponding with the steel extend farther than those corresponding with the lead, as the following measurements, made independently by M. Louis of the Lyons University, show :

	Diameter (mean)	
	of spot.	of penumbra.
Spots (exposed to steel).....	6.4 mm.	11.7 mm.
Spots („ „ „ lead)	7.1 „	10.8 „

It follows therefore that the tempered steel emits *n*-rays, which increase the phosphorescence of the calcium sulphide.

M. A. W.

Transition Resistance and Polarisation at the Aluminium Anode.

FRANZ FISCHER (*Zeit. Elektrochem.*, 1904, 10, 869—877).—An aluminium anode in a solution of sulphuric acid of sp. gr. 1.175 is studied. When the anode is a wire of 2 mm. diameter, its resistance breaks down between 22 and 27 volts. A tube was then tried, the bulb of a thermometer being placed inside it; at about 18 volts, the temperature within the tube had risen to 109°, the electrolyte boiled in contact with it, and the resistance broke down. By using a water-cooled tube as anode, it was possible to raise the voltage to over 200 without a breakdown of the resistance (see also Abstr., 1903, ii, 587). In all cases a distinct film was formed on the anode, and when the

applied *E.M.F.* was increased the current passing increased also, thereafter gradually decreasing to a value which, for a given electrode area, is practically independent of the *E.M.F.*

The greater part of the great fall of potential between the anode and the electrolyte is shown to be due to the low conductivity of the film which forms on the anode and which therefore acts as a condenser.

The thickness of the film formed was measured by means of a microscope and was found to increase in proportion to the potential difference between the electrode and the solution. The thickness with 12 volts was 0.048 mm., with 24 volts 0.105 mm., with 36 volts 0.145 mm., and with 72 volts 0.29 mm.

These observations are satisfactorily explained by supposing that the film grows in thickness until the current which the applied *E.M.F.* can produce is just sufficient to renew it at the same speed as it is dissolved by the sulphuric acid; as the rate of dissolution is constant for a given electrode area, the final current must be independent of the applied *E.M.F.*, as was found to be the case. The formation of the film may be assisted by the fact that alumina, when suspended in aqueous solutions through which a current is passing, always moves towards the anode.

T. E.

Employment of Alternating Currents in Chemistry and the Theory of the Reactions which they determine. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 3, 300—305).—A résumé of work already published (Abstr., 1904, ii, 465).

M. A. W.

Electrolysis by Alternating Currents. ANDRÉ BROCHET and JOSEPH PETIT (*Ann. Chim. Phys.*, 1904, [viii], 3, 433—499).—A résumé of work already published (compare Abstr., 1904, ii, 229, 230, 414; this vol., ii, 27, 28).

M. A. W.

Theory of the Deposition of Metals from rapidly moving Electrolytes. RICHARD AMBERG (*Zeit. Elektrochem.*, 1904, 10, 853—855).—The favourable effects of rapid stirring in electrolytic estimations of metals are, qualitatively, capable of explanation by means of Nernst's theory of reaction velocity in heterogeneous systems (Abstr., 1904, ii, 315).

T. E.

Genesis of Ions by the Motion of Positive Ions and a Theory of the Sparking Potential. JOHN S. TOWNSEND and H. E. HURST (*Phil. Mag.*, 1904, [vi], 8, 738—752).—If a number of ions, n_0 , are set free by the action of ultra-violet light from the negative electrode in a gas and travel in a uniform field to the positive electrode, the total number of ions (n) which arrive is given by the formula: $n = n_0(a - \beta)\epsilon^{(a - \beta)d} / (a - \beta\epsilon^{(a - \beta)d})$, where a is the number of molecules ionised by a negative ion in going through 1 cm. of the gas, β the corresponding number for the positive ion, and d the distance between the parallel electrodes. The values of a and β for given values of pressure p and electric force X may be deduced from determination of currents for different values of d when p and X are constant. If

$\alpha = \beta e^{(a-\beta)d}$, that is, $d = A = (\log \alpha - \log \beta) / (a - \beta)$, then n becomes infinite and $X \times A$ gives the sparking potential. The values $X \times A$ are thus calculated for air and hydrogen at pressures 2 mm., 4 mm., 6 mm., and 8 mm., and compared with the sparking potential determined experimentally; the agreement is very close, being within about 0.5 per cent. in the case of air, and about 1 per cent. in the case of hydrogen. The values found for α and β show that the positive ions in hydrogen are more active in producing ionisation than the positive ions in air. An account of experimental precautions is given, and an addendum by Prof. Townsend is added on the potential required to maintain a current in a gas.

L. M. J.

Diffusion of One Electrolyte in Presence of Another with a Common Ion. UGO GRASSI (*Gazzetta*, 1904, 34, ii, 229—232).—The problem of the diffusion of an electrolyte, B.A., in presence of another, M.A., has been worked out theoretically and tested by Abegg and Bose (Abstr., 1900, ii, 127). The authors derive formulæ for the case where the dissociation is taken into account. These show that, in presence of one of its salts, an acid has a somewhat greater coefficient of diffusion than in the pure solvent.

T. H. P.

Determination of the Relative Velocities of the Ions or Silver Nitrate in Mixtures of the Alcohols and Water and on the Conductivity of such Mixtures. HARRY C. JONES and H. P. BASSETT (*Amer. Chem. J.*, 1904, 32, 409—445. Compare Jones and Lindsay, Abstr., 1903, ii, 55).—The experiments described were carried out with the object of ascertaining the effect of mixtures of methyl alcohol and water on the relative velocities of the ions of a salt, such as silver nitrate. The conductivity of solutions of silver nitrate in water, ethyl alcohol, methyl alcohol, and mixtures of water with each of these alcohols containing 25, 50, and 75 per cent. of the alcohol respectively was determined at 0° and 25°, and the temperature-coefficients of conductivity of the salt in the various solutions were calculated. The results are tabulated and also plotted as curves.

The molecular conductivity in water, ethyl alcohol, and mixtures of these solvents does not show a minimum point either at 25° or 0°, but the curves representing these conductivities indicate that a minimum is approached at 0°. On comparing the conductivities at 0° with those at 25°, it is evident that the influence of one solvent on the other decreases with rise in temperature. In the case of solutions in mixtures of water and methyl alcohol, a minimum point in the conductivity was found both at 25° and 0°.

Determinations were made of the relative velocities at 0° and 25° of the ions of silver nitrate in water, ethyl alcohol, methyl alcohol, and mixtures of methyl alcohol and water containing 25, 50, or 75 per cent. of the former. A comparison is made of the relative temperature-coefficient of ionic mobility for the ions of silver nitrate in water, methyl alcohol, and various mixtures of these solvents, and the temperature-coefficients of mobility of the solvents have been

calculated. The apparatus employed was a modification of that described by Mather (*Abstr.*, 1902, ii, 300). It was found that the difference in the relative velocities in the pure solvents at 0° and 25° decreases as the temperature rises, but with the mixed solvents the opposite is generally the case. The relative velocities depend greatly on the nature of the solvent, and in mixed solvents are found to vary both with the temperature and composition of the mixture.

E. G.

Migration of the Ions in Methyl Alcohol as Solvent. C. DEMPWOLFF (*Chem. Centr.*, 1904, ii, 1376; from *Physikal. Zeit.*, 5, 637—641).—The transport numbers for solutions of potassium chloride, potassium bromide, potassium iodide, lithium chloride, lithium bromide, sodium iodide, sodium methoxide, and silver nitrate have been determined at 19° in a Hittorf's apparatus without diaphragm, using cadmium, platinum, or silver electrodes. The transport numbers of the anions increase with dilution until they reach a constant value. The most dilute solutions were about decinormal. The electric conductivities of solutions of these salts have also been determined at 18°. The results obtained in the case of the iodides are somewhat uncertain. The following table gives the values obtained for the transport numbers of the metallic ion in the case of each compound and the conductivity Λ_{∞} .

Transport No. Λ_{∞} .			Transport No. Λ_{∞} .		
KCl	0.56	92	LiBr	0.45	78
KBr	0.58	98	NaI	0.45	94
KI	0.68	98	NaMeO	0.44	94
LiCl	0.48	77	AgNO ₃	0.56	98

The mean values of the mobility in absolute methyl alcohol were found to be for potassium 54, lithium 37, chlorine 40, and bromine 41. Cadmium and silver salts appear to undergo a process of "alcoholysis" and the values of the conductivity for silver nitrate are therefore too low (mobility of NO₃, 55?). The *E.M.F.* of concentration chains of potassium chloride, potassium bromide, lithium chloride, and lithium bromide have been determined and found to agree with the value calculated from Nernst's equation.

E. W. W.

New Class of Ions. GEORGES MOREAU (*Compt. rend.*, 1904, 139, 916—917. Compare *Abstr.*, 1904, ii, 536).—Air which has been passed through an aqueous salt solution and then through a tube heated at 1000° behaves like an ionised gas, and conducts readily when cooled to 100°. The difference of potential required to produce the maximum current between two electrodes placed in the stream of cooled gas has been measured and the mobility of the ions calculated from this. The positive and negative ions are found to move with the same velocity. Using a solution of definite concentration, the ionic mobility diminishes rapidly as the distance from the source of heat increases; this diminution is not due to fall of temperature, for this was maintained sensibly constant (100—140°). The mobility varies

approximately inversely as the square root of the concentration in the case of the readily ionised potassium salts. The active ions appear to be analogous to those which impart conductivity to the air in the neighbourhood of oxidising phosphorus.

H. M. D.

Use of Helium as Thermometric Substance and its Diffusion through Quartz. ADRIEN JAQUEROD and F. LOUIS PERROT (*Compt. rend.*, 1904, 139, 789—790).—The proposed measurement of high temperatures by means of the expansion of helium in quartz vessels is impossible in consequence of the permeability of the quartz to helium. The rate of diffusion is proportional to the pressure of the gas. At 1100° it is very rapid, and even at about 220° it is perceptible.

H. M. D.

New Form of Pyrometer. NICOLAI S. KURNAKOFF (*Zeit. anorg. Chem.*, 1904, 42, 184—202).—Curves of cooling of antimony, cadmium, bismuth, and tin respectively were investigated by aid of a modified form of the Eschenhagen-Toepfer pyrometer.

A. McK.

Thermal Conductivity of Crystalline Bismuth. F. LOUIS PERROT (*Arch. Sci. Phys. Nat.*, 1904, [iv], 18, 445—457).—The ratio of the conductivity perpendicular to and parallel to the principal axis of crystalline bismuth was found by Senarmont's method to be 1.288, 1.308, 1.408, and 1.390 in the case of four different specimens, of which the first was not so perfect as the other three. The mean of the three last, 1.368, agrees fairly with the single value found by Lownds, 1.42. The author then determined the ratio of the times which elapse between the fusion of two different crystals placed on a cube of bismuth resting on a heated slab of iron when the direction of the flow of heat is (1) perpendicular, and (2) parallel to the principal axes. Crystals melting at 50°, 66°, and 79° were employed; the ratio for crystals 1 and 2 was 1.362, for 1 and 3, 1.373 and 1.370, the mean for all being 1.368.

C. CAILLER (*ibid.*, 457—467) comments on the agreement of the number thus obtained with the ratio of the thermal conductivities, an agreement which is remarkable, inasmuch as the last method does not give the conductivity, and seeks to explain the cause for this agreement in the particular case of bismuth (*Abstr.*, 1902, ii, 466).

L. M. J.

Molecular Depression of the Freezing Point of Water produced by some very Concentrated Saline Solutions. LOUIS C. DE COPPET (*J. Physical Chem.*, 1904, 8, 531—538).—Jones and Getman have shown that for many electrolytes a minimum value for the molecular depression is obtained (*Abstr.*, 1904, ii, 235) in concentrated solution. The author has collected data from his papers on the depression of the freezing point (*Ann. Chim. Phys.*, 1871, [iv], 23, 366; 1872, 25, 502; 26, 98), which show that such a minimum value obtains in the case of solutions of ammonium chloride, sodium chloride,

barium chloride, magnesium sulphate, zinc sulphate, and copper sulphate; no minimum is found in solutions of strontium nitrate, barium nitrate, lead nitrate, and sodium carbonate. In view of the increasing attention to hydrate theories, the author recalls that over 30 years ago he showed that cryoscopic phenomena are explicable by (1) the dissociation of hydrates formed by the solute at the expense of the solvent, (2) dissociation of the solute, probably hydrolytic. L. M. J.

Molecular Depression Constant of *p*-Azoxyanisole. H. MONMOUTH SMITH and W. H. McCLELLAND (*J. Amer. Chem. Soc.*, 1904, 26, 1446—1450).—It has been shown by Gattermann and Ritschke (Abstr., 1890, 1119) that at 116° *p*-azoxyanisole forms a turbid liquid of fluid crystals, which at 134° becomes clear and transparent. Schenck (Abstr., 1898, ii, 286; 1899, ii, 637) has shown that both these transition points undergo abnormally large depressions, and from the depression of the "clear-turbid" transition point, using various solutes, he calculated the molecular depression constant and obtained values ranging from 503 to 859.

In the present investigation, determinations were made of the molecular depression constant of *p*-azoxyanisole, using the following solutes: naphthalene, α -nitronaphthalene, anthracene, *o*- and *p*-acetyl-toluidines, acetamide, phenetole, and cinnamic acid. The average result of 23 determinations gave a value of 562, agreeing fairly well with the value 545 found by Auwers (Abstr., 1900, ii, 262).

Auwers found that when benzil was employed as the solute a value of 860 was obtained. A series of determinations of the molecular depression constant was therefore made using benzil, benzoin, benzophenone, and Michler's ketone respectively as the solute. The average of 12 determinations gave a depression constant of 825.

It has been suggested by Hulett (Abstr., 1899, ii, 468) and de Kock (Abstr., 1904, ii, 548) that the variations in the values found for the molecular depression constant are due to the solubility of the solutes in the fluid crystals, a small difference in the solubility coefficients of the solute in the two modifications of the solvent producing considerable alteration in the depression constant. E. G.

Criticism of Clarke's New Law in Thermochemistry. HARRISON E. PATTEN and W. R. MOTT (*J. Amer. Chem. Soc.*, 1904, 26, 1450—1453. Compare von Loeben, Abstr., 1903, ii, 269).—A discussion of Clarke's paper (Abstr., 1903, ii, 8) on a new thermochemical constant. Curves have been constructed which represent the deviations of this constant from a steady value and compare the heats of combustion calculated by Clarke with the values obtained experimentally by Thomsen. E. G.

Heats of Combustion of Triphenylmethyl and some Triphenylmethane Derivatives. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 732—733).—The following table comprises the thermochemical data recorded in the original paper:

	Heat of combustion at				Heat of formation.	
	Constant vol.		Constant pressure.			
Trinitrotriphenylmethane ...	2272.8	Cal.	2272.9	Cal.	- 32.7	Cal.
Trinitrotriphenylcarbinol ...	2218.3	"	2218.2	"	+ 22.0	"
Triaminotriphenylcarbinol...	2481.0	"	2483.5	"	- 36.3	"
Rosaniline hydrochloride ...	2468.6	"	2471.1	"	+ 10.6	"
Hexamethylrosaniline me- thochloride	3446.0	"	3450.2	"	+ 11.3	"
Triphenylmethyl.....	2377.7	"	2380.0	"	- 71.0	"
Triphenylmethyl peroxide...	4632.8	"	4636.0	"	- 18.0	"
Ditriphenylmethane ethyl acetate.....	5275.9	"	5281.0	"	- 9.0	"

The last three compounds examined were supplied by Gomberg (compare Abstr., 1901, i, 77, 638). M. A. W.

Action of Low Temperatures on Colouring Matters. JULES SCHMIDLIN (*Compt. rend.*, 1904, 139, 731—732).—Alcoholic solutions of rosaniline hydrochloride are solidified at the temperature of liquid air, and the colour of the solid is much less intensely red than that of the solution, but exhibits a beautiful greenish-yellow fluorescence; a similar change is observed with solutions of the salts of hexamethylrosaniline, whilst in the case of eosin the intensity of the red colour as seen by transmitted light is diminished when the solution is solidified in liquid air and the fluorescent colour remains unaltered: these facts are in accordance with Stokes's theory of the difference in origin of fluorescent and transmitted colours.

Solutions of malachite-green or methylene-blue do not undergo any change in colour when cooled in liquid air. M. A. W.

Dilatometric Measurements of Tautomeric Substances. F. GIOLITTI (*Gazzetta*, 1904, 34, ii, 208—220).—Pure ethyl acetoacetate, boiling at 181—181.5°, has the sp. gr. 1.0236 at 15°, which gives a molecular volume of 126.9; this value is not altered by the addition of piperidine or sodium ethoxide. Traube's data (Abstr., 1896, i, 593) give the number 127.9 for the enolic modification and 132.8 for the ketonic form. Dilatometric investigations show that between the temperatures -16° and +100° ethyl acetoacetate does not alter in constitution or else the change is a uniform one and the interval of transformation has its extreme limits outside the above range of temperature.

With acetylacetone, dilatometric measurements between 70° and 95° indicate an increase in the proportion of the ketonic form, which is in agreement with the observations of Perkin (*Trans.*, 1892, 61, 800).

Acetylacetonechloral (Gigli, Abstr., 1899, i, 12) shows, however, no contraction in solution, as would be expected from its behaviour towards ferric chloride and as was shown by Traube (*loc. cit.*) in the case of ethyl acetoacetate.

Physical and chemical methods of detecting tautomeric forms do not, therefore, agree, the results obtained being often uncertain and sometimes contradictory. T. H. P.

Theories on Osmosis, Solubility, and Narcosis. ISIDOR TRAUBE (*Phil. Mag.*, 1904, [vi], 8, 704—715; *Zeit. physiol. Chem.*, 1904, 105, 541—558).—Overton (Abstr., 1897, ii, 337), as the result of a large series of experiments, has evolved the theory that the velocity of osmosis through membranes is determined by the magnitude of the distribution-coefficient between fat and water, and assumes that solution in the fatty substance of the membrane takes place, and that then the substance is passed on from the membrane to the interior of the cell. He has also shown that all the trustworthy narcotics and anæsthetics are rapidly diffusing substances and deduces a theory according to which the efficacy of a narcotic depends principally on its lipoidic solubility. The author urges various objections to these views. Why should not the dissolved substance be more firmly held by the lipoid substance of the membrane? Why does water penetrate membranes more rapidly than anything else? Salts not soluble in fats can penetrate cells. Experiments on diagraphms indicate that the content of lipoid does not determine the sequence of osmotic velocity. The author then states his views, the result of long-continued researches on capillarity constants. The greater the osmotic velocity of a soluble substance, the more it reduces the capillarity constant of water, whilst substances which cannot penetrate the membrane increase the capillarity constant (no exception found). Hence the difference of the surface tensions determines the direction and velocity of osmosis and is the motive force. Applying this to solubility questions, and considering that it is the pure solvent which migrates into the salt solution, it follows that the surface tension of the solution will never fall below that of the solvent—at equality the solution is saturated. It has been found that equal equivalents of substances belonging to homologous series exercising a strong influence on capillarity lower the capillary height of water in the proportion $1 : 3 : 3^2 : 3^3 \dots$. Examples of this are given in the case of the acetates. If methyl alcohol reduces the surface tension of water to a less extent than ethyl alcohol, its tendency to separate from the solution will be less, and hence also its distribution coefficient between a liquid such as benzene and water. Experiments indicate that the distribution-coefficients between benzene, carbon tetrachloride or carbon disulphide, and water for methyl, ethyl, and propyl acetates are also in approximately the ratio $1 : 3 : 9$. Overton's experiments indicate also that this same quantitative relationship holds for the narcotic effect of homologous series (see also Abstr., 1903, ii, 63). L. M. J.

Breaks in the Solubility Curves. WILHELM MEYERHOFFER (*J. Physical Chem.*, 1904, 8, 571—575).—A continuation of the discussion with Ostwald (Abstr., 1903, ii, 280). Gay-Lussac found a break in the solubility curve of Glauber's salt, but he did not establish any connection between the temperature of this and the inversion temperature. He further states in 1839 that the break in the solubility of chlorine hydrate is due to the decomposition, so that above 8° the solubility is that of chlorine, and proceeds: "as for sodium sulphate its decreasing solubility as the temperature rises above

33° can be referred to a decrease in the affinity." It appears clear therefore that Gay-Lussac did not know that Glauber's salt is decomposed at 33° and did not recognise the significance of the break.

L. M. J.

Liquid Crystals. ALFRED COEHN (*Zeit. Elektrochem.*, 1904, 10, 856—857).—If a liquid is suspended in another and an *E.M.F.* be applied to the emulsion, then the liquid with the smaller dielectric constant will move towards the anode. The author has attempted to discover, by the application of this fact, whether turbid *p*-azoxyanisole is a mixture of two substances. No movement could be detected. He points out, however, that no movement would occur in a mixture of two substances having the same dielectric constant, and that the movement would not be observed in a mixture of two substances in equilibrium provided that the disturbance of equilibrium caused by the movement was compensated sufficiently rapidly.

It was also found impossible to effect any separation of the turbid liquid by centrifugal force.

When *p*-azoxyanisole is frequently heated above the temperature at which it becomes clear and allowed to solidify, a dark coloured substance collects in the tube; this may point to the presence of an impurity.

T. E.

The Colloidal State. G. E. MALFITANO (*Compt. rend.*, 1904, 139, 920—922).—The author considers that matter in the colloidal state represents a system composed of a dissociated electrolyte with insoluble molecules grouped around the ions.

H. M. D.

Composition of Colloidal Granules. VICTOR HENRI and ANDRÉ MAYER (*Compt. rend.*, 1904, 139, 974—976. Compare Abstr., 1904, ii, 243, 325).—According to Duclaux (compare Abstr., 1904, ii, 162, 243, 325), the precipitate that is formed on mixing solutions of A equivalents of $K_4Fe(CN)_6$ and a equivalents of $CuSO_4$ ($A > a$) always contains a certain quantity, β , of potassium ferrocyanide; the author has calculated from Duclaux's numbers the values of the ratio $\beta/(A - a - \beta)$, the partition coefficient of the $Fe(CN)_6$ between the liquid and the precipitate for a fixed value of a , and finds that it diminishes in proportion as A increases. The composition of the colloidal precipitates examined by Duclaux may therefore be regarded as particular cases of adsorption (compare van Bemmelen, Abstr., 1900, ii, 338, 466; Biltz, Abstr., 1904, ii, 392), the granules being formed of copper ferrocyanide which has adsorbed a certain quantity of potassium ferrocyanide.

M. A. W.

Determination of the Size of Molecules from the Kinetic Theory of Gases. J. H. JEANS (*Phil. Mag.*, 1904, [vi], 8, 692—699).—The size of molecules may be determined from observations on (1) viscosity of gases, (2) conduction of heat by gases, (3) coefficient of diffusion of gases, (4) deviations from Boyle's law, and (5) volume occupied by matter in the solid and liquid states. In all these, the constant N , that is, number of molecules in 1 c.c. of gas

at normal temperature and pressure, also enters, and 1, 2, 3 yield values for NS^2 , whilst 4, 5 give NS^3 , where S is the diameter of the molecule considered as a sphere. Hence, from observations of either class, N or S may be determined. The value for N is better obtained, however, by electrical methods, and different experiments yield values of about 4×10^{19} . Using this as the value for N , the following values are obtained for $S \times 10^8$:

	Viscosity.	Conduction.	Diffusion.	Boyle's law.	Mean.
Hydrogen	2.05	1.99	2.03	2.05	2.03
Helium	1.81	—	—	—	1.81
Water vapour.....	3.39	—	—	—	3.39
Carbon monoxide ...	2.90	2.74	2.92	—	2.86
Ethylene.....	3.77	3.88	—	—	3.81
Nitrogen.....	2.90	2.74	—	3.12	2.91
Nitric oxide	2.82	2.81	—	—	2.82
Oxygen	2.81	2.58	2.71	—	2.73
Argon	2.79	—	—	—	2.79
Carbon dioxide	3.47	3.58	3.27	3.00	3.36
Nitrous oxide.....	3.54	3.48	—	—	3.52
Ethyl chloride	4.68	—	—	—	4.68
Chlorine	4.11	—	—	—	4.11

In calculating the mean, double weight is assigned to the viscosity determinations, which are probably the most accurate. L. M. J.

Possibility of Chemical Reaction. ROBERT DE FORCRAND (*Compt. rend.*, 1904, 139, 905—908).—If q denotes the heat development associated with the irreversible transformation of a system from the same original to the same final condition, q' the corresponding heat change in the isothermal reversible transformation, then $q - q' > 0$ is the general condition for the possibility of the change. The author criticises the utility of this thermodynamic relationship in practice, and arrives at the conclusion that the thermochemical rule, $q > 0$, is the only really practical criterion of the possibility of chemical change. H. M. D.

Prediction of Chemical Reactions. ROBERT DE FORCRAND (*Compt. rend.*, 1904, 139, 908—911. Compare preceding abstract).—If q represents the quantity of heat developed when a system changes from the condition A to the condition B , q_1 that for the change from the condition A to the condition B_1 , and if q' and q'_1 are the heat changes for the corresponding isothermal reversible transformations, then the actual chemical change which takes place, assuming that the external work is sensibly equal to zero, will be from A to B_1 if $q_1 - q'_1 > q - q'$ or $q_1 - q - (q'_1 - q') > 0$. This relationship is termed the principle of maximum transformable heat. It is pointed out that for most chemical reactions $q'_1 - q_1$ is small in comparison with $q_1 - q$, and

the principle then passes into the principle of maximum work, $q_1 - q > 0$. The author considers that the application of the simplified inequality is the only practical method available for the prediction of chemical change.

H. M. D.

Free Energy of Formation. HANS VON JÜPTNER (*Zeit. anorg. Chem.*, 1904, **42**, 235—249. Compare Abstr., 1904, ii, 549).—Theoretical.

A. McK.

Dynamic Isomerism. THOMAS LOWRY (*Brit. Assoc. Reports*, 1904, 1—32).—This report contains a general survey of the subject of dynamic isomerism, comprising: 1, an historical introduction; 2, a discussion of the nature of dynamic isomerism and of the influence of catalytic agents on the equilibrium; 3, a review of the principal classes of compounds exhibiting such isomerism classified according to the nature of the intermolecular changes taking place; and discussions of: 4, optical inversion; 5, the behaviour of dynamical isomerides towards reagents; 6, their physical relations, including freezing point curves, crystallography, mutarotation, refraction, magnetic rotation, electrical conductivity, colour, absorption spectra, and luminosity; and, 7, reversible polymeric change. Very full references to the literature are given.

C. H. D.

Magnitude of the Equilibrium of the same Reaction in Different Solvents. LEO PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1070—1081).—The equilibrium constant of the reaction $2\text{KCl} + \text{Hg}_2\text{SO}_4 \rightleftharpoons \text{Hg}_2\text{Cl}_2 + \text{K}_2\text{SO}_4$ has the same value whether the solvent is water, 20 per cent. aqueous alcohol, or 61.5 per cent. aqueous glycerol. The temperature-coefficient (between 25° and 44.2°) of the *E.M.F.* of the element,

$$\frac{\text{Hg}|0.01n - \text{KCl}, \text{Hg}_2\text{Cl}_2|n - \text{KNO}_3}{n - \text{KNO}_3} \frac{\text{Hg}_2\text{SO}_4, 0.01n - \text{K}_2\text{SO}_4|\text{Hg}}{n - \text{KNO}_3},$$

has the same value in the first two of the above three solvents, but in 61.5 per cent. aqueous glycerol the coefficient is considerably greater. The change in the magnitude of the constant produced by adding alcohol or glycerol to the solution indicates a diminution in the degree of dissociation of the reacting compounds. This, taken together with the non-coincidence found between the constant in the above solvents and that calculated for KCl and K_2SO_4 in these solvents, indicates that the degree of dissociation of these substances is less in glycerol or alcohol than in water.

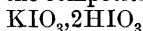
T. H. P.

Ozone. I. Equilibrium between Ozone and Hydrochloric Acid. STEPHAN JAHN (*Zeit. anorg. Chem.*, 1904, **42**, 203—212).—If a current of ozonised oxygen be passed through dilute hydrochloric acid, it carries with it from the solution chlorine with a partial pressure corresponding with the concentration of hydrogen and chlorine ions in the solution, if the equilibrium in the liquid phase is established sufficiently quickly. Colloidal platinum was used as a catalyser. Ozone

alone acts very slowly on 0.05*N* hydrochloric acid, but on the addition of colloidal platinum the conductivity of the solution quickly diminishes. From this diminution of conductivity, the partial pressure of the chlorine liberated can be calculated, whilst the value for the conductivity at any given time indicates the concentration of the solution at that particular time. The amount of chloric acid formed in the solution was so small that it did not interfere with the potential measurements made.

A. McK.

The System: Potassium Iodate, Iodic Acid, and Water at 30°. P. A. MEERBURG (*Chem. Centr.*, 1904, ii, 1362; from *Chem. Weekblad*, i, 474—479. Compare Abstr., 1902, ii, 495; 1904, ii, 112).—The solubility of mixtures of potassium iodate and iodic acid in varying proportions has been determined at 30°. Solutions which contain 9.51 per cent. of the iodate or 76.70 of iodic acid are saturated at this temperature. Compounds of the composition $\text{KIO}_3, \text{HIO}_3$ and



may separate from solution. The former salt can be crystallised from water at 30°, but not the latter. The compound $\text{KIO}_3, 2\text{HIO}_3$ is only deposited from solutions containing an excess of iodic acid. The stability of these compounds is about the same at the ordinary temperature as at 30°.

E. W. W.

Determinations in the System: Cupric Chloride, Ammonium Chloride, and Water. P. A. MEERBURG (*Chem. Centr.*, 1904, ii, 1362—1363; from *Chem. Weekblad*, i, 551—559. Compare preceding abstract).—The conditions of equilibrium of aqueous solutions containing cupric chloride and ammonium chloride have been determined at 30°. A saturated solution of ammonium chloride at 30° contains 29.5 per cent., and a saturated solution of the dihydrate of cupric chloride, $\text{CuCl}_2, 2\text{H}_2\text{O}$, 48.95 per cent.; under other conditions, the only compound which separates in a solid state is the double salt, $\text{CuCl}_2, 2\text{NH}_4\text{Cl}, 2\text{H}_2\text{O}$. In the original paper, the experimental data are plotted out in curves; the three solubility curves cut one another in two quadruple points. A compound $\text{CuCl}_2, \text{NH}_4\text{Cl}, \text{H}_2\text{O}$ does not exist; a mixture of the dihydrate of cupric chloride with the double salt mentioned above has probably been mistaken for a compound of this composition. The cupric ammonium chloride dihydrate is stable between -11° and $+80^\circ$. The ice curve and the dihydrate curve intersect at the cryohydric point $\pm -11^\circ$.

E. W. W.

Kinetics of the Reaction between Potassium Permanganate and Oxalic Acid. ANTON SKRABAL (*Zeit. anorg. Chem.*, 1904, 42, 1—59. Compare Abstr., 1903, ii, 684).—It is first shown that the action of potassium permanganate on an excess of oxalic acid in the presence of sulphuric acid is a unimolecular reaction, represented by $[\text{Mn}(\text{OH})_3, \text{C}_2\text{H}_2\text{O}_4] \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$. The oxidation of oxalic acid is caused by the manganic ions and accordingly the reaction just expressed takes place in two stages, thus: $[\text{Mn}(\text{OH})_3, \text{C}_2\text{H}_2\text{O}_4] \rightarrow \text{Mn}^{\text{III}}$ and $\text{Mn}^{\text{III}} + \text{C}_2\text{H}_2\text{O}_4 \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$. Investigation of the action of equivalent amounts of manganese salts, in the form of phosphate and

acetate respectively, on oxalic acid did not indicate that a reaction of a higher order took place. When the concentration of the oxalic acid is increased, or when the total reaction mass is diluted so that the volume is double the original volume, the velocity coefficients in the reaction $[\text{Mn}(\text{OH})_2, \text{C}_2\text{H}_2\text{O}_4] \rightarrow \text{Mn}^{+++}$ are not altered. The reaction $\text{Mn}^{+++} + \text{C}_2\text{H}_2\text{O}_4 \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$ accordingly takes place at a rate so rapid that it cannot be measured. Only the former action, that is, the rate of the electrolytic dissociation of the manganese salt, can be measured; it is a reaction of the first order, and the velocity coefficients are constant only when the concentration of oxalic acid is constant.

The action of potassium permanganate on oxalic acid in the presence of manganous salts was studied. At first, the rate of oxidation of the oxalic acid is slow. As the reaction proceeds, manganic salt is formed accompanied by a vigorous induced oxidation of the oxalic acid and followed by the reaction of the first order just mentioned. The intermediate formation of manganic ions was recognised.

Manganese peroxide exhibits towards oxalic acid a behaviour similar to that of potassium permanganate.

The reaction between permanganate and oxalic acid takes place in the following stages, thus: (*Incubation period*) (1) $\text{C}_2\text{H}_2\text{O}_4 + \text{KMnO}_4 \rightarrow \text{Mn}^{+++} + \text{CO}_2$ (measurable), (2) $\text{C}_2\text{H}_2\text{O}_4 + \text{Mn}^{+++} \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$ (practically instantaneously); (*Induction period*) (3) $\text{Mn}(\text{OH})_2 + \text{KMnO}_4 \rightarrow \text{Mn}^{+++}$ (less quickly than the former stage), (4) $\text{Mn}^{+++} + \text{C}_2\text{H}_2\text{O}_4 \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$ (practically instantaneously), (5) $\text{Mn}^{+++} + \text{C}_2\text{H}_2\text{O}_4 \rightarrow [\text{Mn}(\text{OH})_3, \text{C}_2\text{H}_2\text{O}_4]$ (practically instantaneously), (6) $\text{Mn}^{+++} \rightarrow \text{Mn}(\text{OH})_2 + \text{Mn}(\text{OH})_4$ (practically instantaneously); (*End period I*) (7) $[\text{Mn}(\text{OH})_3, \text{C}_2\text{H}_2\text{O}_4] \rightarrow \text{Mn}^{+++}$ (measurable), (8) $\text{C}_2\text{H}_2\text{O}_4 + \text{Mn}^{+++} \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$ (practically instantaneously); (*End period II*) (9) $\text{Mn}(\text{OH})_2 + \text{Mn}(\text{OH})_4 \rightarrow \text{Mn}^{+++}$ (less quickly than the former stage), (10) $\text{C}_2\text{H}_2\text{O}_4 + \text{Mn}^{+++} \rightarrow \text{Mn}(\text{OH})_2 + \text{CO}_2$ (practically instantaneously).

The rate of stage (1) increases with increase of amount of acid present. Stage (4) is conditioned by the rate at which the ions Mn^{+++} are formed in stage (3). In presence of manganese sulphate, the incubation period is not observed, whilst the measurable reaction in the induction period proceeds very quickly. If the conditions for the formation of complex manganic salts are favourable, that is, if the concentration of oxalic acid is great and that of hydrogen ions small, stage (5) proceeds more quickly than any other stage in the induction period, and the end period is expressed by (7) and (8). Otherwise, stage (6) is the most rapid in the induction period and the end period is expressed by (9) and (10).

A. McK.

"Primary Oxide" Theory of Oxidation. ANTON SKRABAL (*Zeit. anorg. Chem.*, 1904, 42, 60—86. Compare preceding abstract).—A theoretical paper. The deductions are based on (1) Ostwald's law of successive reactions, (2) Luther's thermodynamic conclusions respecting substances with several oxidation stages, (3) the assumption that all reactions are more or less ionic, (4) the kinetic conception of chemical equilibrium, and (5) the phenomena observed during many oxidation processes. Primary oxide ions are formed during processes of

oxidation and reduction, and are characterised by their being decomposed according to the experimental conditions into two oxidation stages. All oxidation processes can be resolved into "primary reactions." "Irrespective of whether a process of oxidation is measurable, immeasurable, quick or immeasurably slow, the reduction of the primary oxide ions by acceptors and the decomposition of the primary oxide ions into two extreme stages or their conversion into complex or undissociated compounds will proceed more quickly than the primary reactions, which cause the formation of primary oxide ions." A. McK.

Study of Reversible Oxidation and Reduction Reactions in Solutions. EUGENE P. SCHOCH (*J. Amer. Chem. Soc.*, 1904, 26, 1422—1433).—An investigation has been carried out with the object of determining the influence of the concentrations of their components on the equilibrium in solutions of iodine, potassium ferrocyanide, potassium ferricyanide, and potassium iodide acidified with $N/20$ hydrochloric acid. The reaction is probably simple and takes place according to the equation $2\text{Fe}(\text{CN})_6''' + \text{I}_2 \rightleftharpoons 2\text{Fe}(\text{CN})_6'' + 2\text{I}'$.

Although the potassium ions and the hydrochloric acid take no part in the reaction, it is necessary to know the influence of their concentration, and for this purpose a series of *E.M.F.* measurements was made.

In order to ascertain the influence of the different members of the reaction on the chemical equilibrium, the concentrations necessary for one equilibrium were first determined; then, whilst two of the substances were kept constant, the concentration of the third was varied, and the quantity of the fourth required to restore equilibrium was determined experimentally. The results are tabulated.

It was found that the formula for equilibrium in such solutions at constant temperatures is
$$\frac{C^4 (\text{ferrocyanide}) \times C (\text{free iodine})}{C^2 (\text{ferricyanide}) \times C^2 (\text{potassium iodide})} = K.$$

The presence in this formula of the fourth power of the concentration of the ferrocyanide instead of the second power is proved to be correct both by the *E.M.F.* measurements and the chemical equilibrium determinations. E. G.

Oxidation Phenomena. GEORG KASSNER (*Zeit. angew. Chem.*, 1904, 17, 1851—1856).—A lecture delivered to the pharmacological section of the Gesellschaft deutscher Naturforscher und Aerzte in Breslau, 1904. A. McK.

Hydration and Hardening. PAUL ROHLAND (*Zeit. Elektrochem.*, 1904, 10, 893—900).—Hydration reactions, whether organic or inorganic, take place spontaneously, and their velocity is very much affected by small quantities of foreign substances and by temperature.

Hardening does not always accompany hydration (quicklime, for example, falls to powder); it is therefore due to some special circumstance. The author believes that a solid solution is formed in all cases in which hardening accompanies hydration.

The catalytic acceleration or retardation of hydration by salts is

regarded as a result of a change of the solubility of the solid substance which is undergoing hydration. T. E.

Limits of Sensitiveness of Odours and Emanations. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1904, [viii], 3, 293—295). A résumé of work already published (Abstr., 1904, ii, 554).

M. A. W.

Use of Quartz Vessels for Lecture Experiments. EMIL FISCHER (*Ber.*, 1904, 37, 4603—4605).—Quartz vessels, the cost of which is one-tenth of that of platinum, are recommended for use in demonstrating the evolution of oxygen from nitric acid, and the formation of water. E. F. A.

An Improved Kipp's Apparatus. RICHARD J. FRISWELL (*Chem. News*, 1904, 90, 154—155).—The apparatus has the usual three bulbs of an ordinary Kipp's apparatus. A central tube, reaching nearly to the bottom of the lower bulb, is ground in the lower part of the top bulb and fixed with marine glue. Above the junction, the tube is widened out somewhat and rises in the top bulb to about three-fourths of the height of the latter. The bottom bulb is filled with a concentrated solution of zinc sulphate, ferrous chloride, or calcium chloride (according to the material placed in the middle bulb) to within about half an inch of the top. The acid from the top bulb passes down the central tube when the tap on the delivery tube is opened, and rises to the surface of the concentrated solution, where it comes into contact with the materials in the middle bulb. When the tap is closed, some of the heavy solution is forced up into the acid bulb, where it sinks through the lighter acid and may be drawn off, as it accumulates, by a tap which is provided for the purpose. As the economical working depends on the different densities of the fresh and exhausted acids, care must be taken to avoid mixing the strata of liquids, either by shaking when moving or by the effervescence caused by scraps of marble, &c., falling into the lower bulb. W. P. S.

A Cheap Kipp's Apparatus. FRANK SOUTHERDEN (*Chem. News*, 1904, 90, 286—287).—The apparatus consists of an ordinary "lime tower" down the centre of which passes a wide glass tube loosely fitting the constriction at the lower part of the tower. The top of the latter is closed by a doubly bored cork, through one hole of which is passed the neck of a large funnel, whilst the second hole carries the tap delivery tube of the apparatus. The neck of the funnel is connected by a piece of india-rubber tubing to a narrow glass tube passing down the wide tube and reaching to the bottom of the tower. The funnel serves as the acid-container and the part of the tower above the constriction is filled with ferrous sulphide, marble, &c., according to the gas which it is desired to produce. W. P. S.

New Gas-evolution Apparatus. S. BOSNJAKOVIĆ (*Zeit. anal. Chem.*, 1904, 43, 624—625).—A very simple apparatus, consisting of two glass bulbs connected by channels. The whole is made of one

piece of glass. The solid reagent is placed in one of the bulbs, and when the apparatus is in one position the liquid reagent is in the other, but by tilting the vessel through 90° , the liquid comes in contact with the solid and evolution of gas commences. The evolution is arrested by reverting to the first position. M. J. S.

New Hydrogen Sulphide, Carbon Dioxide, or Hydrogen Generating Apparatus. H. ARZBERGER (*Chem. Centr.*, 1904, ii, 1358—1359; from *Pharm. Post*, 37, 581).—An apparatus for the generation of hydrogen sulphide, carbon dioxide, or hydrogen is described in which the solid iron sulphide, calcium carbonate, or zinc is contained in a Soxhlet tube fitted with an india-rubber bung through which three holes are bored. The acid, which, in the case of hydrogen sulphide, consists of a 20—25 per cent. solution of sulphuric acid or preferably hydrochloric acid, is added drop by drop from a tap funnel, the stem of which passes through one hole of the bung. The exhausted acid runs off automatically through the siphon into a flask which is fitted to the Soxhlet tube, and from this vessel it may be removed by a tap. The solid may be washed with water after use by means of a second funnel to which a tap and tube are attached, the latter passing through the second hole in the bung. The gas escapes by a tube which is inserted in the third hole of the bung, and is connected with a suitable washing apparatus. E. W. W.

Inorganic Chemistry.

Reduction of Perchlorate by the Wet Method. B. SJOLLEMA (*Zeit. anorg. Chem.*, 1904, **42**, 127—128).—Potassium perchlorate, when boiled in aqueous solution with ferrous hydroxide in the absence of free alkali, is reduced quantitatively to chloride. A. McK.

Rate of Crystallisation of Plastic Sulphur. JOSEPH H. KASTLE and WALTER PEARSON KELLEY (*Amer. Chem. J.*, 1904, **32**, 483—503).—The rate of change of plastic sulphur into the crystalline variety has been studied by sp. gr. and dilatometric methods.

A specimen of sulphur was heated to 200° and poured into cold water; one portion was left in water at the ordinary temperature, whilst another was kept in water at 70°; the sp. gr. of each was determined at intervals of an hour. In another experiment, the sulphur was heated to 444° before being poured into water; portions of this specimen were kept at 80°, 60°, and 40° respectively, whilst another portion was left in cold water; the sp. gr. was determined at intervals in each case. The results indicate that the rate of change of plastic into crystalline sulphur varies according to the temperature to which the sulphur is heated before being poured into water, and also with

the temperature at which the product is preserved. The higher the initial temperature to which the sulphur is heated, the slower is the crystallisation; and the higher the temperature at which the sulphur is kept, the more rapid is the change.

In another series of experiments, a specimen of plastic sulphur was divided into five portions which were kept under water, dilute ammonia, 95 per cent. alcohol, dilute bromine water, and *N*/10 iodine solution respectively, the sp. gr. being determined at intervals in each case. It was found that ammonia, alcohol, and bromine accelerate, whilst iodine retards, the crystallisation.

A study of the effect of heat has shown that plastic sulphur has no definite melting point, the effect of any increase of temperature being merely to diminish its viscosity and to increase its tendency to pass into the crystalline form.

The stability of any particular specimen of plastic sulphur can be judged from its colour; light amber-coloured specimens crystallise easily, whilst reddish-brown varieties remain plastic for longer periods. Experiments have shown that when the plastic and orthorhombic forms of sulphur are heated at 120—125° for a sufficient length of time they become alike in colour, a state of chemical equilibrium being ultimately reached in each case.

Experiments made with the object of determining the effect of tension on the crystallisation showed that specimens of sulphur under tension crystallise more rapidly than those not under tension.

Determinations of the rate of change by the dilatometric method showed that plastic sulphur prepared by pouring into water sulphur that has been heated only to a moderately high temperature crystallises rapidly, whereas that which has been heated to near the boiling point before being poured into water crystallises very slowly. The velocity of the change of plastic into crystalline sulphur begins comparatively rapidly, about 10 per cent. of the total change taking place in the first 30 minutes, and then gradually diminishes. This gradual decrease in the rate of crystallisation indicates that several molecular forms are present in the supercooled liquid, some of which change to the crystalline variety of the element more rapidly than others. E. G.

The Chlorides of Sulphur. Sulphur Tetrachloride and its Compounds. OTTO RUFF (*Ber.*, 1904, 37, 4513—4521. Compare Ruff and Fischer, *Abstr.*, 1903, ii, 204).—The author has re-examined the double compounds of sulphur tetrachloride described in the literature, and has corrected some erroneous analyses. The so-called sulphur dichloride was employed in the preparations, and the author's view is confirmed that this substance is a solution of largely dissociated sulphur tetrachloride in sulphur chloride.

Sulphur tetrachloride, prepared by the slow combination of sulphur chloride with liquid chlorine in a sealed tube, is a yellowish-white substance, melting at -30.5° to -31° to a red liquid. Its dissociation pressure reaches 1 atmosphere at a few degrees above its melting point. Water decomposes it in a sealed tube almost quantitatively, forming sulphurous acid.

The double compounds of sulphur tetrachloride are designated by their formulæ.

[With GEORG FISCHER.]—The compound $\text{SCl}_4\cdot\text{SbCl}_5$, prepared by adding sulphur chloride to a cold solution of antimony pentachloride in sulphuryl chloride and draining by means of the apparatus described by Ruff and Plato (*Ber.*, 1901, 34, 1749), forms slender, white needles melting at $125\text{--}126^\circ$ in an atmosphere of chlorine in a sealed tube to a yellow liquid, and subliming at 150° . Water decomposes it vigorously. No solid compound could be obtained from sulphur tetrachloride and phosphorus pentachloride.

The salt, $\text{SCl}_4\cdot\text{TiCl}_4$ crystallises in slender, yellow needles, often radially grouped, melts at $62\text{--}64^\circ$ in an atmosphere of chlorine, sublimes at about 100° , and dissolves in sulphuryl chloride, chloroform, carbon disulphide, or light petroleum.

$2\text{SCl}_4\cdot\text{SnCl}_4$ forms large, yellow crystals, melts at 37° , and decomposes at about 40° . It fumes in air, but is more stable than the titanium compound, and dissolves readily in chloroform, light petroleum, sulphuryl chloride, carbon disulphide, phosphorus oxychloride, ether, or benzene. The corresponding compound with zirconium tetrachloride is very unstable, and could not be isolated in a pure form. A silicon compound could not be obtained.

[With EINBECK.]— $\text{SCl}_4\cdot\text{FeCl}_3$, prepared in phosphorus oxychloride solution, forms a yellow, crystalline precipitate, decomposing rapidly on warming. The compound $2\text{FeCl}_3\cdot\text{POCl}_3$ was obtained on warming the constituents together on the water-bath in the form of a bright yellow, crystalline mass.

[With GEORG FISCHER.]— $\text{SCl}_4\cdot 2\text{ICl}_3$ forms yellow crystals, decomposing without fusion on even slight warming. No compounds could be obtained from arsenic trichloride, antimony trichloride, or chromic chloride.

[With KURT THIEL.]— $\text{SCl}_4\cdot 2\text{AsF}_3$ forms yellow crystals and only attacks glass slowly, but decomposes or chars thionyl chloride, carbon tetrachloride, carbon disulphide, alcohol, ether, benzene, or light petroleum.

No compounds were obtained from antimony, tin, or titanium fluorides, or from the chlorides of uni- or bi-valent metals.

C. H. D.

Theory of the Lead Chamber Process. II. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1904, 17, 1777—1785).—Polemical. A reply to A. McK.

Catalytic Phenomena in the Preparation of Persulphuric Acid. G. I. PETRENKO (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1081—1088).—The yield of persulphuric acid obtained by the electrolysis of sulphuric acid is dependent on the use of a platinum anode which apparently oxidises and then exerts a catalytic action, diminishing the yield of the peracid. The yield of the latter is almost doubled by the addition of hydrochloric acid. With an iridium anode, the yield is considerably less than with platinum, and the iridium goes into solution more readily than platinum.

T. H. P.

Ultramicroscopical Observations. I. Separation of Sulphur from Thiosulphuric Acid and of Selenium from Selenious Acid. WILHELM BILTZ and WILLY GAHL (*Chem. Centr.*, 1904, ii, 1367; from *Nachr. K. Ges. Wiss. Göttingen*, 1904, 300—310).—By means of Raehlmann's ultramicroscope, homogeneous or "optically empty" solutions may be more readily distinguished from turbid solutions, and the phenomena of precipitation more closely followed. By means of the arrangement used, a field of 0.00004 cm. was illuminated. Filtration, or contact with cover glasses or india-rubber, destroys the optical homogeneity of solutions. Distilled water must be rendered clear before distilling, and must be protected from access of air during distillation and afterwards. A Pukall cell may be used for filtration, the air which enters the filter being made to pass through cotton-wool.

Thiosulphuric acid decomposes as soon as it is formed, the non-dissociated acid being the less stable. By means of the ultramicroscope, it has been shown that the process of decomposition is not "continuous," the discontinuity becoming apparent at about the same time as the opalescence is visible to the naked eye. Colourless, supersaturated solutions of the acid in water can, therefore, exist. Colloidal aqueous solutions of the acid appear to be blue, and are extremely unstable. The action of sulphurous acid on selenious acid has also been found to be optically discontinuous.

E. W. W.

Colloidal Tellurium. IV. ALEXANDER GUTBIER (*Zeit. anorg. Chem.*, 1904, 42, 177—183. Compare Abstr., 1902, ii, 653; 1904, ii, 613).—A detailed account of results already published.

A. McK.

Action of Hydrogen Peroxide on Tellurium. ALEXANDER GUTBIER and F. RESENSCHECK (*Zeit. anorg. Chem.*, 1904, 42, 174—176. Compare Gutbier and Wagenknecht, Abstr., 1904, ii, 613).—When hydrogen peroxide is added to a solution of tellurium in concentrated aqueous potassium hydroxide, telluric acid is produced in small yield.

A. McK.

Apparatus for Separating Nitrogen Quickly and Completely from a Mixture of Gases containing it. FERDINAND HENRICH (*Zeit. angew. Chem.*, 1904, 17, 1755—1757).—An apparatus is described by means of which nitrogen is separated automatically from a mixture of gases containing it, the mixed gases being repeatedly passed over heated copper and copper oxide, soda lime, phosphoric oxide, and a heated mixture of magnesium and quicklime. A full description is appended to the sketch of the apparatus in question.

A. McK.

Formation of Nitric Oxide at High Temperatures. WALTHER NERNST (*Chem. Centr.*, 1904, ii, 1368; from *Nachr. k. Ges. Wiss. Göttingen*, 1904, 261—276. Compare Muthmann and Hofer, Abstr., 1903, ii, 206).—If a system which is in equilibrium at a high temperature is rapidly cooled, the composition of the mixture at the lower

temperature will not accurately represent the condition at the higher, since the cooling cannot be effected instantaneously. In all cases, no matter in which direction the composition of the gaseous mixture deviates from that of the equilibrium state, the proportion of the product formed at the higher temperature will be too small, except for a small temperature interval in which the curve calculated from thermodynamical data touches that obtained from observed values. In cases in which it is impossible to allow sufficient time for the state of equilibrium to be attained because the temperature is too low and the velocity of the action too small, the velocities of the opposing reactions may be measured by experiments on streams of gas at different velocities. The concentration at which both reactions have the same velocity, and hence the equilibrium constant, may be calculated. When gases are brought to very high temperatures for a very short time, as, for instance, when a mixture of hydrogen and oxygen in the proportions contained in water is exploded with air and the mixture rapidly cooled, an examination of the products of the explosion may serve, under certain conditions, to ascertain the conditions of equilibrium at such temperatures.

A litre of air was passed through platinum or iridium tubes and the nitric oxide absorbed in sulphuric acid. The temperature was estimated by means of a thermo-element or a photometer. At temperatures above 1700° , equilibrium was attained when one litre passed through the tube in 20 minutes. At 1760° , the equilibrium concentration of the nitric oxide was found to be 0.64 per cent. by volume and at 1922° 0.97 per cent. The "heat-toning" of the reaction calculated from these data is 45,600 cals., whilst the value found by experiment was 43,200. A state of equilibrium could not be obtained in the platinum furnaces at 1538° . The velocities of the opposing reactions show that the reaction is bimolecular and that the equilibrium concentration of the nitric oxide is 0.37 per cent. by volume. From Bunsen's determinations of the decrease of volume caused by exploding mixtures of hydrogen and oxygen with air, it has been calculated that at 3500° the mixture contains about 5 per cent. by volume of nitric oxide when equilibrium is established. Under the ordinary atmospheric pressure, the time required to convert half the nitrogen of air into nitric oxide is about 100 seconds at 1540° and 3.5 at 1737° . The following table shows the observed and calculated equilibrium constants χ at temperatures from 1500 — 3200° :

Temp. (abs.).	χ observed.	χ calculated.
1811°	0.37	0.35
2033°	0.64	0.67
2195°	0.97	0.98
3200°	about 5	4.4

E. W. W.

Preparation of Yellow Arsenic. ALFRED STOCK and WERNER SIEBERT (*Ber.*, 1904, 37, 4572—4575).—A special form of apparatus is described and figured by means of which arsenic is sublimed in a vacuum and the vapour immediately cooled by liquid air. Under

these conditions, a yellow modification of arsenic is deposited, which, when exposed to light, is instantly converted into the black modification. A similar change takes place in the dark, when the yellow form is allowed to assume the ordinary temperature, but the change is not accompanied by any luminescence phenomena. E. F. A.

The Preparation of Pure Boron Trifluoride and Silicon Tetrafluoride and some Physical Constants of these Compounds. HENRI MOISSAN (*Compt. rend.*, 1904, 139, 711—714).—Boron trifluoride, prepared by heating a mixture of boron trioxide, calcium fluoride, and sulphuric acid, and purified by passing through cylinders containing sodium fluoride and finally by solidifying in a vacuum (compare Abstr., 1903, ii, 642), melts at -127° and boils at -101° (compare Abstr., 1904, ii, 331); the corresponding constants of the synthetical compound are -126° and -99° respectively.

Silicon tetrafluoride, similarly prepared and purified, and also the synthetic compound, solidifies at -97° under atmospheric pressure, and volatilises without passing through the liquid stage (compare Olszewski, Abstr., 1884, 816) under a pressure of 2 atmospheres. Silicon tetrafluoride melts at -77° to a transparent, mobile liquid, which boils at -65° under 181 cm. pressure; the critical temperature is -1.5° , and the critical pressure 50 atmospheres. M. A. W.

Action of Boric Acid on the Alkali Peroxides. Formation of Perborates. GEORGE F. JAUBERT (*Compt. rend.*, 1904, 139, 796—798).—When an intimate mixture of 248 grams of boric acid and 78 grams of sodium peroxide is gradually added to 2 litres of cold water, a clear solution is first obtained from which the perborate, $\text{Na}_2\text{B}_4\text{O}_8 \cdot 10\text{H}_2\text{O}$, crystallises after a time in 90 per cent. yield. The aqueous solution of the perborate contains free hydrogen peroxide. Its solubility at 11° , 22° , and 32° was found to be 42, 71, and 138 grams per litre. The perborate cannot be recrystallised from its aqueous solution.

When a quantity of hydrochloric acid equivalent to half the sodium in the perborate is added to this solution, a perborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, separates in the form of white crystals which are very stable at the ordinary temperature and are not affected by atmospheric carbon dioxide. This salt is less soluble than the first perborate; its aqueous solution slowly decomposes at 50 — 60° and evolves oxygen rapidly at 100° . The solution has all the properties of hydrogen peroxide, and on account of its stability in the air the crystalline salt may conveniently be used as a means of obtaining an aqueous solution of hydrogen peroxide. H. M. D.

Tension of Carbon Dioxide in Sea Water and the Reciprocal Influence of the Carbon Dioxide of the Sea and of the Atmosphere. AUGUST KROGH (*Compt. rend.*, 1904, 139, 896—898).—The ocean contains about 6.55×10^{16} kilograms of carbon dioxide in the form of readily dissociated salts or twenty-seven times the quantity contained

in the atmosphere, and the variation of this quantity with the pressure is expressed in the following table :

Pressure per cent.	Quantity in kilos.
0.01	4.57×10^{16}
0.02	5.89×10^{16}
0.03	6.55×10^{16}
0.04	7.04×10^{16}
0.05	7.36×10^{16}

A series of determinations of the tension of carbon dioxide in the sea and in the atmosphere has given the following results : (1) in the north of the Atlantic Ocean, the tension of carbon dioxide is much lower in the water than in the atmosphere ; (2) the atmosphere over the Atlantic Ocean and its shores contains less carbon dioxide (0.029 per cent.) than in Central Europe (0.033 per cent.) ; (3) in the southern hemisphere, where the ocean covers the major part, the atmosphere contains less carbon dioxide than in the northern hemisphere (0.026 per cent.). It follows, therefore, that the percentage of carbon dioxide in the atmosphere is increasing, and that the sea compensates for the increase by absorbing the gas.

M. A. W.

Action of Potassium Cyanide Solution on Various Metals.
 ANDRÉ BROCHET and JOSEPH PETIT (*Bull. Soc. chim.*, 1904, [iii], 31, 1255—1257. Compare Abstr., 1904, ii, 229, 230, and 414).—Aluminium and magnesium are readily attacked in the cold by potassium cyanide solution, copper and zinc less readily, yielding respectively the salts $\text{Cu}_2(\text{CN})_2 \cdot 6\text{KCN}$ and $\text{Zn}(\text{CN})_2 \cdot 2\text{KCN}$ and other metals very slowly except on heating. Cadmium and silver are attacked by potassium cyanide solution in presence of oxygen, but mercury is unaffected, and the amalgamation of a metal retards the action of the salt on it.

Deville and Debray (*Compt. rend.*, 1876, 82, 241) and Glaser (Abstr., 1903, ii, 242) have shown that platinum dissolves in solutions of potassium cyanide. The author finds that this does not occur unless the solution of the cyanide is heated, and that the effect is diminished by polishing the platinum.

T. A. H.

Action of Potassium Cyanide on Metallic Electrodes.
 ANDRÉ BROCHET and JOSEPH PETIT (*Bull. Soc. chim.*, 1904, [iii], 31, 1257—1261. Compare Abstr., 1904, ii, 229, 230, and 414).—Most metals behave as soluble anodes when placed in potassium cyanide solution under the influence of an alternating current. A number of metals, including copper, zinc, silver, and cadmium, dissolve quantitatively when the current is weak. Nickel dissolves quantitatively so long as the current does not exceed 2 amperes per sq. decimetre ; beyond this, the dissolution diminishes, reaching a minimum of 80 per cent. of the theoretical when the current density is 8 amperes per sq. decimetre (compare Le Blanc and Schick, Abstr., 1904, ii, 230). Cobalt dissolves irregularly, and the anode becomes pitted. Mercury is almost immediately covered by a black precipitate which prevents

further action, but amalgamation has no effect on the dissolution of copper and zinc. Lead is almost without action.

Silver begins to deposit on the cathode almost as soon as it appears in the electrolyte, and cadmium behaves similarly, but copper, zinc, and nickel deposit only with difficulty, whilst with cobalt and iron no deposition occurs.

The observation of Glaser (Abstr., 1903, ii, 242) that platinum is dissolved when employed as a cathode in potassium cyanide solution is confirmed, and it is shown that the action is much more marked when barium cyanide is employed as the electrolyte. This dissolution of platinum under these conditions is due to the disintegration of the cathode, probably with the transitory formation of an alloy with the alkali metal and the dissolution in the electrolyte of the finely-divided platinum particles so liberated (compare Bredig and Haber, Abstr., 1899, ii, 78; Haber and Sack, Abstr., 1902, ii, 441; Bran, *ibid.*, ii, 442). In favour of this view is the slow evolution of hydrogen which takes place from the cathode immediately after the current has been stopped.

T. A. H.

Theory of the Dissolution of Metals in Potassium Cyanide Solution under the Influence of an Alternating Current.

ANDRÉ BROCHET and JOSEPH PETIT (*Bull. Soc. chim.*, 1904, [iii], 31, 1261—1265. Compare preceding abstracts).—Such metals as silver, which are quantitatively dissolved from the anode and deposited on the cathode, are insoluble in potassium cyanide solution under the action of an alternating current. On the contrary, copper, zinc, nickel, and cobalt, which are either not deposited or deposited only with difficulty, are soluble in potassium cyanide solution. The cases of iron and platinum, which behave as insoluble anodes and slightly soluble cathodes, and yet are readily dissolved by potassium cyanide solution under the action of an alternating current, are not so easily explicable. Platinum also dissolves in the cyanide solution under the action of a continuous current frequently interrupted, and it is probable that its dissolution is due to disintegration while it momentarily acts as a cathode, the dissolution of the detached particles being facilitated by the oxidising action of the platinum electrode immediately afterwards functioning as an anode.

The original paper contains a series of curves showing (a) the influence of current frequency (from 5 to 100 per second) on the rate of dissolution of various metals, and (b) the simultaneous influence of current density and frequency on the rate of dissolution of nickel. The first set of curves shows that as the frequency is increased, copper dissolves less quickly, whilst iron, nickel, and cobalt exhibit a maximum and then diminish; with platinum, the maximum is unattainable under these conditions. The second series of curves appears to show that nickel behaves like copper when the current density is less than 7 amperes per sq. decimetre, but above this behaves like iron, and that when frequency and density are simultaneously and sufficiently increased no solution should occur. The latter deduction is not in harmony with the experimental observation recorded in the preceding abstract.

T. A. H.

Reactions between Salts in Non-aqueous Solutions. II. In Acetone. ALEXANDER NAUMANN [and, in part, with WILHELM EIDMANN, MAX MÜLLER, PAUL SCHULZ, and ERNST VOIGT] (*Ber.*, 1904, **37**, 4328—4341. Compare *Abstr.*, 1904, ii, 819).—Pure anhydrous acetone of sp. gr. 0·795 at 18°/4° was used. The following salts are readily soluble: aluminium bromide, ammonium bromide, trichromate, iodide, nitrate, perchlorate, and thiocyanate; antimony tribromide, chloride (0·186), and iodide; barium bromide and iodide; bromine; cadmium bromide (64·5), chlorate, iodide (4), and nitrate; caesium nitrate; calcium bromide, chlorate, dichromate, iodide, and nitrate; cerium bromide, chloride, iodide, and nitrate; chromic nitrate; chromic anhydride; ferric chloride (1·59) and nitrate; ferrous chloride; erbium nitrate; iodine; potassium bromide, chlorochromate, ferricyanide, ferrocyanide, iodide, permanganate, mercuri-iodide, and thiocyanate; cobalt chloride (36·4), bromide, iodide, and nitrate; cupric bromide, chloride (34·7), and chlorate; lanthanum nitrate; lithium bromide, chloride, iodide, and nitrate; magnesium bromide, chlorate, chloride, and iodide; palladous chloride; platinic chloride; mercuric chloride (0·7), bromide, and nitrate; rubidium nitrate; sulphur; silver nitrate (227) and nitrite; thalious nitrate; uranium bromide; uranyl chloride, iodide, and nitrate; bismuth trichloride (5·59) and tri-iodide; zinc chloride (2·3) and iodide; stannous chloride (1·8); stannic chloride, bromide, and iodide. The numbers in brackets indicate the number of grams of acetone required to form a saturated solution with 1 gram of the salt at 18°.

The following salts are very sparingly soluble: aluminium chloride and nitrate; ammonium chromate, diborate, and thiosulphate; barium chlorate and nitrate; lead bromide and nitrate; cadmium chloride; calcium chloride; potassium nitrate; lithium diborate; sodium dichromate; mercuric iodide; rubidium bromide; strontium chloride and nitrate; thallic chloride; thorium nitrate.

A list of some 197 insoluble compounds is given.

Ammonia yields precipitates with acetone solutions of the following salts: cupric, bismuth, antimony, cobaltous, mercuric, stannous, and zinc chlorides, silver nitrate, cadmium bromide, and cadmium iodide. The precipitates in all cases are additive compounds of the salt and ammonia.

The following yield precipitates of silver haloids with silver nitrate in acetone solution: bismuth, antimony, ferric, cobaltous, mercuric, strontium, and zinc chlorides, cadmium bromide and iodide. Hydrogen sulphide precipitates the metals of stannous chloride, bismuth chloride, silver nitrate, and cadmium bromide as sulphides. It precipitates mercuric chloride as $\text{HgCl}_2 \cdot 2\text{HgS}$, and cadmium iodide as $\text{CdI}_2 \cdot 2\text{CdS}$. Double decomposition has been observed between cadmium bromide and mercuric chloride, cupric chloride and calcium bromide, bismuth chloride and potassium iodide, mercuric chloride and cadmium iodide, mercuric chloride and bismuth iodide, and also between potassium thiocyanate and solutions of the following salts: zinc chloride, silver nitrate, and cobalt chloride.

Cupric, ferric, and mercuric chlorides are reduced by stannous chloride. Ferric and cupric chlorides are reduced by potassium iodide, and ferric chloride partially by hydrogen sulphide.

Acetone solutions of silver nitrate yield precipitates with hydrogen chloride, bromide, or iodide, and, in the case of the bromide and iodide, the precipitate dissolves in an excess of the acid. Silver nitrate and sulphur yield Ag_2S_2 .

Mercuric chloride and cuprous bromide yield mercurous bromide, cuprous chloride, and chlorine; cadmium bromide is decomposed by an acetone solution of chlorine, and cuprous chloride, which is insoluble in acetone, yields, with an acetone solution of chlorine, cupric chloride, with bromine, a mixture of cupric chloride and bromide, and with an iodine solution, cuprous iodide and cupric chloride. Mercurous chloride, suspended in acetone, is only slightly affected by chlorine, but with bromine and iodine yields mixtures of mercuric chloride with the bromide and iodide.

J. J. S.

Reactions between Salts in Non-aqueous Solutions. III. ALEXANDER NAUMANN [and JOHANNES SCHROEDER] (*Ber.*, 1904, 37, 4609—4614. Compare Abstr., 1904, ii, 819).—The solubility of a large number of inorganic salts in pyridine was determined qualitatively. The compound $\text{HgCl}_2 \cdot \text{C}_5\text{H}_5\text{N}$, prepared by the addition of mercuric chloride to pyridine, crystallises in needles. Its behaviour, when dissolved in pyridine, towards ammonia, hydrogen sulphide, and stannous chloride is similar to that of mercuric chloride. With ammonium thiocyanate and silver sulphate it gives precipitates of ammonium chloride and mercuric sulphate respectively.

The compound $\text{CuCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, prepared by the addition of cupric chloride to pyridine, separates from alcohol in needles. Its behaviour and that of the compound $\text{AgNO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$ (in pyridine solution) and of a solution of silver sulphate in pyridine towards various reagents is described in considerable detail.

A. McK.

Sodamide and certain of its Reaction Products. W. PHILLIPS WINTER (*J. Amer. Chem. Soc.*, 1904, 26, 1484—1512).—A convenient method is described for the preparation of sodamide.

When sodamide is exposed to dry air, it slowly assumes a yellowish-brown colour and is found to contain nitrous and hyponitrous acids.

When sodamide is decomposed by water, hydrogen and nitrogen are produced. The relative proportions of these gases vary with the condition of the sodamide. It has been found that the proportion of hydrogen is high in the case of sodamide which has been insufficiently heated owing to the presence of unchanged sodium, but is low when the sodamide has been properly prepared. Nitrogen is always evolved to a small extent and is formed in larger proportion from sodamide which has been kept for some time than from freshly prepared specimens. The production of the nitrogen is probably due to the presence in the sodamide of sodium azoimide or some analogous compound formed by oxidation of ammonia either in the process of manufacture of the sodamide or during its exposure to dry air.

If finely powdered sodamide is sprinkled into a vessel containing water heated nearly to boiling through which a current of carbon

dioxide is being passed, a shower of brilliant sparks is produced and a solution of disodium cyanamide is formed.

When sodamide is treated with phosphorus pentachloride, a violent reaction takes place and a white sublimate is produced which consists of ammonium chloride, sodium chloride, traces of phosphorus compounds, and a small quantity of a *substance* insoluble in water. This insoluble compound cannot be isolated, but when the soluble substances are removed from the sublimate by means of nitric or acetic acid, a white, nearly tasteless, odourless *compound*, PO_2N or $\text{PH}_2\text{O}_2\text{N}$, is obtained, which is not affected by hot strong mineral acids.

When sodamide is warmed with yellow phosphorus, an energetic reaction occurs, and the product consists of sodium phosphide and other substances, including oxy-acids of phosphorus and probably an amide of phosphorus.

E. G.

Supercooled Fusions and Solutions of Sodium Thiosulphate. STEWART W. YOUNG and J. P. MITCHELL (*J. Amer. Chem. Soc.*, 1904, **26**, 1389—1413).—Sodium thiosulphate pentahydrate exists in three forms: the ordinary commercial or α -form, the β -form described by Parmentier and Amat (*Abstr.*, 1884, 819), and the γ -form discovered in the course of the present investigation. The β -form is obtained most readily by heating the α -form at 80 — 100° for a few minutes in a sealed glass tube and cooling to -10° or -20° , when the product solidifies in long needles. The γ -form is produced occasionally instead of the β -form; the conditions necessary for its formation have not been fully investigated, but it appears that the presence of a small excess of water in the tube favours its production. This γ -modification is obtained as a compact, opaque mass which melts at a little above 0° , whilst the β and α -forms melt at about 32° and 49° respectively. Each of these forms on melting is converted into a saturated solution and a lower hydrate.

Four different lower hydrates are described. The α -form is obtained when the α -pentahydrate is melted and left at the ordinary temperature for a day or two. The b -form is produced by the partial fusion of the α -form, the d -form by the partial fusion of the β -pentahydrate, and the c -form by the partial fusion of the γ -pentahydrate.

A large number of experiments have been made with the object of ascertaining the conditions under which these various forms are produced from supercooled solutions and fusions, attention being paid particularly to the form of the thiosulphate from which the solution or fusion was prepared, the rate at which the tubes were cooled, the temperature to which they were heated, and the length of time for which the heating was continued. For the details of these experiments and the results obtained, the original must be consulted.

In order to afford an explanation of the results of this investigation, a hypothesis is put forward based on that proposed by Jaffé (*Abstr.*, 1903, ii, 469), which ascribes the initiation of the crystallisation to the presence of nuclei. It is suggested that these nuclei consist of fragments of crystalline aggregates left in the liquid after the breaking down of the crystalline structure and that, under certain conditions,

they unite to form crystalline aggregates which are capable of starting the crystallisation. E. G.

Composition and Solubility of the Hydrates of Sodium Thiosulphate. STEWART W. YOUNG and W. E. BURKE (*J. Amer. Chem. Soc.*, 1904, **26**, 1413—1422. Compare preceding abstract).—Considerable difficulty was experienced in determining the composition of the various hydrates of sodium thiosulphate owing to the fact that all the other forms are metastable with respect to the α -form and are rapidly converted into this form if a trace of it is present. Parmentier and Amat (Abstr., 1884, 819) have shown that the β -form consists of a pentahydrate. There is little doubt that the γ -form is also a pentahydrate, although hitherto it has not been analysed. Analyses have been made of the α -, b -, and d -forms, which show that the first two consist respectively of a monohydrate and a dihydrate and that the d -form is probably a tetrahydrate. The composition of the c -variety has not been ascertained.

Determinations of the solubility of these different hydrates have given the following results, which are expressed as the number of parts of the anhydrous salt, $\text{Na}_2\text{S}_2\text{O}_3$, in 100 parts of water. The solubility of the α -form of sodium thiosulphate is 59.69 at 10° , 70.07 at 20° , 75.90 at 25° , 82.45 at 30° , 91.24 at 35° , 103.37 at 40° , and 123.87 at 45° . In the case of the β -form, the values obtained were 97.55 at 20° , 108.98 at 25° , 119.69 at 28° , 126.50 at 29.5° , and 130.26 at 30° . The solubility of the α -form is 163.92 at 20° , 168.32 at 25° , and 174.20 at 30° . For the b -form, the values found were 122.68 at 20° , 127.43 at 25° , 133.27 at 30° , 138.84 at 35° , 144.92 at 40° , and 165.11 at 50° . In the case of the d -form, the solubility was found to be 141.48 at 33.5° , 153.23 at 36.2° , and 168.82 at 38.6° . The solubilities of the γ - and c -forms have not been determined. These solubility data have been plotted as curves which are of particular value as defining exactly the ranges of supercooling and supersaturation of the forms studied.

E. G.

Formation and Constitution of Bleaching Powder. NAZARENO TARUGI (*Gazzetta*, 1904, **34**, ii, 254—260).—The author finds that the formation of bleaching powder containing a maximum amount of active chlorine is influenced by the presence of oxygen. When lime is completely hydrated and left in contact with air, after some time it exhibits the reactions of peroxides—blue coloration with guaiacum resin, red coloration with ferrous sulphate and potassium thiocyanate, and blue coloration with chromic acid and ether. In the formation of bleaching powder, the chlorine acts on the water yielding hydrogen chloride and oxygen, the latter then converting a part of the lime into calcium peroxide: $4\text{Cl} + 2\text{H}_2\text{O} = 4\text{HCl} + \text{O}_2$; $\text{CaO}, \text{H}_2\text{O} + \text{O}_2 = \text{CaO}_2, \text{H}_2\text{O}_2$; $\text{CaO}_2, \text{H}_2\text{O}_2 + 2\text{HCl} = \text{CaO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$.

The author's experiments indicate that hypochlorites must, in general, be regarded as chlorides of peroxides, and that bleaching powder containing 44.09 per cent. of chlorine (which is the maximum proportion obtainable in the commercial product) is the chloride of

calcium peroxide *plus* 1 mol. of water, $\text{Ca}(\text{OCl})_2 \cdot \text{H}_2\text{O}$. This constitution for bleaching powder is in accord with its action on mercury, which is converted quantitatively into mercuric chloride: $\text{CaO}_2\text{Cl}_2 + \text{Hg} = \text{CaO}_2 + \text{HgCl}_2$. This method is the subject of a patent for the manufacture of corrosive sublimate. T. H. P.

Action of Water on the Phosphates of Calcium. FRANK K. CAMERON and ATHERTON SEIDEL (*J. Amer. Chem. Soc.*, 1904, 26, 1454—1463. Compare Rindell, *Abstr.*, 1902, ii, 208).—A study has been made of the extent to which the three calcium phosphates are decomposed by water, and experiments have been made to ascertain the effect of calcium sulphate, calcium carbonate, and carbon dioxide on the hydrolysis. Since tricalcium phosphate and monocalcium phosphate always contain an excess of either base or acid, the results of the solubility determinations cannot be regarded as of absolute value, but are useful as indicating the nature of the reaction between the phosphates and water.

In each experiment, a weighed quantity of the phosphate was placed in a bottle with distilled water and maintained for several weeks at 25° with occasional shaking. Portions of the clear solutions were withdrawn and the amounts of calcium and phosphoric acid in them were estimated. The results show that tricalcium and monocalcium phosphates both undergo considerable decomposition, but that dicalcium phosphate is more stable and only slightly decomposed by water. In the case of the mono- and tri-calcium phosphates, the amount of decomposition and the concentration of the resulting solution are found to depend on the relative proportions of phosphate and water employed.

In presence of calcium sulphate, the amount of phosphoric acid dissolved from tricalcium phosphate is increased. A slight increase also takes place with monocalcium phosphate, but a considerable decrease occurs in the amount of phosphoric acid dissolved from the dicalcium salt.

In presence of calcium carbonate, the amount of phosphoric acid dissolved is decreased in all three cases.

Carbon dioxide causes an increased quantity of phosphoric acid to be dissolved from tri- or di-calcium phosphate, but is without effect on the action of water on the monocalcium salt. E. G.

Action of Amalgams on Solutions. GUSTAVE FERNEKES (*J. Physical Chem.*, 1904, 8, 566—570).—A reply to some criticisms by G. McP. Smith (*Abstr.*, 1904, ii, 400) of the author's explanation of the action of amalgams on water (*Abstr.*, 1904, ii, 163). The author adds the results of some further experiments. It was first shown that barium is not replaced in its amalgam by either sodium or potassium when acted on by a concentrated solution of a salt. It was found, however, that barium amalgam reacts with water about three times as quickly as with a solution of potassium chloride. This is readily explicable on Kahlenberg's theory, as each molecule of the salt would influence the surrounding water molecules. Molecular quantities of

sodium and potassium chlorides were also allowed to act on sodium amalgam for 15 minutes, at the end of which time the amalgam was found to contain only potassium; this fact and also the anomalous behaviour of sodium hydroxide solutions are not explicable by the ionic theory. L. M. J.

Equilibrium in the System $\text{GlO}:\text{SO}_3:\text{H}_2\text{O}$. CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1904, 26, 1433—1446).—It is found that the only definite hydrated sulphates of glucinum are $\text{GlSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{GlSO}_4 \cdot 2\text{H}_2\text{O}$, no evidence being obtainable of the existence of the heptahydrate described by Klatzo (*Zeit. Chem.*, 1869, 12, 129). The tetrahydrate has an aqueous vapour pressure equal to or greater than the pressure of its own water of crystallisation; it has been found by tensimeter experiments that this pressure over phosphoric oxide at 20° is equivalent to 20 mm. of olive oil, and increases rapidly with the temperature. The dihydrate is stable in the air at the ordinary temperature, but loses water slowly at 100 — 110° . The anhydrous sulphate cannot be obtained quite pure on account of the difficulty of removing the last traces of water without incurring the loss of sulphur trioxide.

An examination of the various so-called basic sulphates of glucinum has shown that these substances are not definite compounds, but consist of solid solutions of the sulphate in the hydroxide. E. G.

Zincum Boricum or Oxyboricum. E. HOLDERMANN (*Arch. Pharm.*, 1904, 242, 567—568).—When a solution of zinc sulphate and another of borax are mixed in varying proportions, the second solution containing also just enough sodium hydroxide to complete the conversion of the sulphate into sodium sulphate, the filtrate gives no further precipitate with either solution when the zinc sulphate and borax have been mixed in the proportion of 3 : 2 mols. The composition of the precipitate, therefore, is $\text{Zn}_3(\text{B}_4\text{O}_7)_2(\text{OH})_2$. C. F. B.

The Complexity of Dissolved Sulphates. ALBERT COLSON (*Compt. rend.*, 1904, 139, 857—859. Compare Abstr., 1904, ii, 377, 532).—A solution of copper sulphate containing 0.75 gram-mol. in 2 litres gave a depression of the freezing point of 0.70° , whilst the sulphuric acid solution, obtained by exactly precipitating the copper in the same solution by hydrogen sulphide, gave a depression of 1.51° , at least twice 0.70° ; it follows, therefore, that the second solution contains twice as many molecules as the first, and the molecular complexity of copper sulphate in solution is represented by the formula $(\text{CuSO}_4)_2$, and similar results were obtained in the case of magnesium sulphate. The author suggests that the sulphates of the bivalent metals in aqueous solution have the formula $(\text{HSO}_4\text{M})_2\text{O}$, and may be regarded as being formed by the condensation of 2 mols. of sulphuric acid with the hydroxide, $(\text{OH}\cdot\text{M})_2\text{O}$; this explains the acidic nature of the metallic sulphates. On the other hand, the metallic hydroxides are sufficiently strong bases to displace sodium or ammonium hydroxide from solutions of their sulphates, for when a solution of sodium sulphate is added to zinc oxide neutral to phenolphthalein suspended in water, the mixture becomes increasingly alkaline towards the indi-

cator owing to the liberation of sodium hydroxide and the formation of the basic salt, $\text{SO}_4(\text{Zn}\cdot\text{O}\cdot\text{ZnOH})_2$; similarly, a blue coloration is developed when copper oxide is added to a solution of ammonium sulphate.

M. A. W.

A New Cause of Dissociation of Mercuric Chloride and its Influence on the Antiseptic Properties of Solutions of Corrosive Sublimate. HENRI VITTENET (*Bull. Soc. chim.*, 1904, [iii], 31, 1133—1138).—When equal parts of ammonium and mercuric chlorides are dissolved in tap-water, there slowly forms a precipitate, which is at first white and has the composition $\text{N}(\text{HgCl})_3$, but on further standing gradually becomes yellow. The production of this substance was traced to the presence of acid carbonates in the water, and its formation was found to be inhibited by previous ebullition of this. When the two salts are dissolved in distilled water to which sodium hydrogen carbonate or carbonate has been added, the precipitate formed is white and has the composition $\text{N}(\text{HgCl})_3\cdot 3\text{NH}_4\text{Cl}$, but gradually becomes yellow when washed with water, and the final product is bright yellow and has approximately the composition required by the formula $\text{N}(\text{Hg}\cdot\text{OH})_2\cdot\text{Hg}\cdot\text{OCl}$. The formation of these precipitates in such solutions used as antiseptic baths leads to a diminution of efficiency, and it is suggested that in preparing these the water should first be boiled or the ammonium chloride should be replaced by sodium chloride; with either of these precautions, no precipitation occurs. T. A. H.

Yttrium Earth related to Gadolinium. GEORGES URBAIN (*Compt. rend.*, 1904, 139, 736—738).—By means of three separate methods of fractional crystallisation, the author has obtained from the yttrium earths 100 grams of a rare earth, which consists chiefly of the oxide of Lecoq de Boisbaudran's new element $\text{Z}\delta$ (compare Abstr., 1896, ii, 249; also Demarçay, Abstr., 1900, ii, 656). The methods employed were: (i) Fractional crystallisation of the double nitrates of the rare earths and of nickel. The fractions containing the element $\text{Z}\delta$ were intermediate between those of gadolinium and dysprosium. (ii) Fractional crystallisation of the nitrates of the earths in the presence of bismuth nitrate (compare Abstr., 1904, ii, 37, 43, 173; also Demarçay, Abstr., 1900, ii, 347). The nitrate of $\text{Z}\delta$ has the same solubility as bismuth nitrate. (iii) Fractional crystallisation of the ethyl sulphates of the rare earths (compare Abstr., 1900, ii, 346). The earth thus separated exhibits only the absorption band $\lambda = 488$ characteristic of $\text{Z}\delta$, but this does not preclude the possibility of $\text{Z}\delta$ being a mixture of elements some of which possess no absorption spectra. M. A. W.

Neodymium Oxide. ANTON WAEGNER (*Zeit. anorg. Chem.*, 1904, 42, 118—126. Compare Abstr., 1903, ii, 729).—That very varying statements have been made as to the colour of neodymium oxide, Nd_2O_3 , is probably due to the oxide under investigation having been in many cases contaminated with other rare earths, and particularly with praseodymium.

The crude neodymium chloride used by the author, which contained traces of praseodymium and lanthanum, was converted into the

oxalate; this, when carefully heated in a platinum boat in a current of oxygen, formed a pink residue from which carbon dioxide could be obtained at a higher temperature. When the oxalate is heated at a bright red heat, an oxide of the probable composition Nd_4O_7 is formed; prepared in this manner, it is brownish-pink and resembles Brauner's oxide, Nd_2O_4 , in being converted by prolonged heating with the blowpipe or in a current of hydrogen into the oxide Nd_2O_3 . Further, its brown tint is due to a trace of praseodymium peroxide, since, when heated moderately in a current of hydrogen, the traces of praseodymium peroxide are reduced to sesquioxide, and the true colour of the neodymium oxide, namely, a sky-blue colour with a violet tint, is rendered evident.

The existence of a higher neodymium oxide was also rendered probable by the spectrometric observations with the two oxides. The spectrum from the oxide Nd_2O_3 is quite different from that of the oxide Nd_4O_7 .
A. McK.

Deposition of Aluminium from Ethyl Bromide Solution. HARRISON E. PATTEN (*J. Physical Chem.*, 1904, 8, 548—565).—It has been shown by Plotnikoff (*Abstr.*, 1902, ii, 639) that aluminium bromide dissolved in ethyl bromide yields a conducting solution from which aluminium may be deposited, and the author has further studied this deposition. In a 4.38 per cent. solution, no aluminium was deposited even with currents of fairly high density; evidence was, however, obtained of the formation of protective films on the aluminium, and this in a solution which was almost perfectly free from oxygen. In a solution of 40.95 per cent. of aluminium bromide, aluminium was deposited when the current density reached 0.0023 ampere per sq. cm.; the electrolytic metal reacts on the solution vigorously, a gas, probably butane, being evolved; below the current density given, the rate of dissolution exceeds that of deposition. The potential of the aluminium against the solution was 1.10 volts, and that of the bromine was -1.20 volts. Using the aluminium as anode, further evidences of film formation were obtained, but no high counter-pressures were obtained.

During the work, aluminium bromide was obtained in the form of large, rhombohedral crystals of a pale yellow colour. L. M. J.

Stimulating and Paralysing Influences of certain Substances in the Production of Rust. LÉON LINDET (*Compt. rend.*, 1904, 139, 859—862).—The catalytic action exercised by certain metals on the oxidation of organic compounds has been studied by Livache (*Abstr.*, 1883, 756; 1884, 532), by Trillat (*Abstr.*, 1903, i, 222; ii, 201, 589; 1904, ii, 38), and by Duchemin and Dourlen (*Abstr.*, 1904, i, 961). The author finds that the rusting of iron is accelerated by the presence of copper, and retarded by such metals as tin, lead, zinc, manganese, aluminium, or magnesium; the phenomena are to be attributed to the hydroxide of the metal which dissolves in the water, for similar stimulating or paralysing effects are produced on the iron by water which has been in contact with the metal. Arsenic and its compounds exercise a paralysing effect on the rusting of iron, and when present in large quantities stop it altogether; in this case the dissolved

iron hydroxide forms colloidal, ferrous, or ferric arsenite. Soluble salts such as the chlorides and sulphates of the alkali metals have a stimulating effect on the rusting of iron, probably due to their electrolytic dissociation, whilst among organic substances such compounds as sugar, phenol, or resorcinol stimulate the formation of rust; alcohol or methyl salicylate has a retarding effect, and acetic or salicylic acid dissolves the iron as rapidly as it is oxidised. M. A. W.

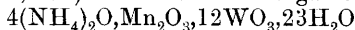
Colloidal Ferric Hydroxide. A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1067—1069).—The colloidal ferric hydroxide examined was prepared by saturating a solution of ferric chloride with ammonium carbonate and purifying the solution obtained by dialysis. The liquids thus prepared contain as much as 5.3 grams of ferric oxide per litre, but no iron ions are present; the solution also contains chlorine, probably in combination with ammonia. On electrolysis, or with electrolytes such as barium hydroxide, potassium thiocyanate, hydrochloric acid, zinc sulphate, &c., the solution is coagulated, but with mercuric or mercurous nitrate or ferric chloride it forms first a complex colloid; besides this, salts of mercury or copper convert a part of the iron into salts of their acids. By ammoniacal solution of copper oxide, the colloid is precipitated together with cupric oxide, whilst in the presence of organic hydroxy-acids and on heating, the cupric oxide is reduced to cuprous oxide; the same occurs with ammoniacal silver oxide solution. When the solution is boiled with Fehling's solution, the colloid is precipitated together with cuprous oxide. T. H. P.

Perchromic Acid and the Perchromates. HORACE G. BYERS and E. EMMET REID (*Amer. Chem. J.*, 1904, 32, 503—513).—The blue compound produced when chromic acid is treated with hydrogen peroxide has been the subject of numerous investigations, and various formulæ have been assigned to it. Recently Patten (*Abstr.*, 1903, ii, 431) has stated that this substance is not perchromic acid, but that the chromium is present in the chromous state.

When the ethereal solution of the blue compound is treated with potassium at -20° , hydrogen is evolved and a purplish-black precipitate is produced. This compound, which has the composition KCrO_4 or $\text{K}_2\text{Cr}_2\text{O}_8$, is unstable, and rapidly decomposes with evolution of oxygen and formation of potassium dichromate. By the addition of an alcoholic solution of potassium cyanide to the blue solution, Wiede (*Abstr.*, 1898, ii, 295) obtained a similar compound to which he ascribed the formula $\text{KCrO}_5 \cdot \text{H}_2\text{O}_2$. When the blue solution is prepared without employing an excess of hydrogen peroxide, the compound obtained on the addition of potassium cyanide has the same composition as that produced by the action of potassium. The corresponding sodium, ammonium, lithium, magnesium, calcium, barium, and zinc salts were prepared.

A study of the blue ethereal solution has shown that it contains perchromic acid, $\text{H}_2\text{Cr}_2\text{O}_8$. When the solution is prepared in presence of an excess of hydrogen peroxide, it is probable that a more highly oxidised compound is also produced. E. G.

Derivatives of Complex Inorganic Acids. ALLEN ROGERS and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1904, **26**, 1474—1484. Compare Abstr., 1903, ii, 375).—Ammonium manganitungstate,

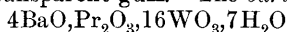


(Brubaker, *Thesis*, 1904), prepared by boiling ammonium paratungstate and manganic hydroxide with water, forms large, red, octahedral crystals and is very soluble in water.

Ammonium nickelitungstate, $3(\text{NH}_4)_2\text{O}, \text{Ni}_2\text{O}_3, 16\text{WO}_3, 22\text{H}_2\text{O}$, obtained by boiling the hydrated sesquioxide of nickel with an ammoniacal solution of ammonium paratungstate, forms a greenish-white crystalline powder and is sparingly soluble in water. On adding barium chloride to a solution of this salt, *barium nickelitungstate*, $19\text{BaO}, \text{Ni}_2\text{O}_3, 16\text{WO}_3$, is produced as a white precipitate. When ammonia is passed into the solution of ammonium nickelitungstate, another *ammonium* salt, $(\text{NH}_4)_2\text{O}, \text{Ni}_2\text{O}_3, 4\text{WO}_3, 7\text{H}_2\text{O}$, is obtained which is dark blue when moist, but of a light blue colour when dry.

The following compounds were prepared by boiling the respective hydroxides with an aqueous solution of ammonium paratungstate for 8 hours, filtering, and evaporating the filtrate to dryness on the water-bath. When dry, all the salts were quite insoluble.

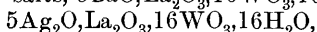
Ammonium praseodymitungstate, $2(\text{NH}_4)_2\text{O}, \text{Pr}_2\text{O}_3, 16\text{WO}_3, 16\text{H}_2\text{O}$, is obtained as a green, transparent gum. The *barium* salts,



and $6\text{BaO}, \text{Pr}_2\text{O}_3, 16\text{WO}_3, 9\text{H}_2\text{O}$, form white powders. The *silver* salt, $4\text{Ag}_2\text{O}, \text{Pr}_2\text{O}_3, 16\text{WO}_3, 8\text{H}_2\text{O}$, is of a greenish-white colour.

Ammonium neodymitungstate, $3(\text{NH}_4)_2\text{O}, \text{Nd}_2\text{O}_3, 16\text{WO}_3, 20\text{H}_2\text{O}$, and the *barium* salt, $6\text{BaO}, \text{Nd}_2\text{O}_3, 16\text{WO}_3, 17\text{H}_2\text{O}$, are of a pink colour.

Ammonium lanthanitungstate, $2(\text{NH}_4)_2\text{O}, \text{La}_2\text{O}_3, 16\text{WO}_3, 16\text{H}_2\text{O}$, and the *barium* and *silver* salts, $5\text{BaO}, \text{La}_2\text{O}_3, 16\text{WO}_3, 16\text{H}_2\text{O}$ and



form white powders.

Ammonium ceritungstate, $2(\text{NH}_4)_2\text{O}, \text{Ce}_2\text{O}_3, 16\text{WO}_3, 2\text{H}_2\text{O}$, is obtained as a red, transparent glass. E. G.

Uranyl Chloride. WILLIAM GECHSNER DE CONINCK (*Ann. Chim. Phys.*, 1904, [viii], **3**, 500—506. Compare Abstr., 1901, ii, 164).—Aqueous solutions of uranyl chloride have the following sp. gr. :

Percentage of dissolved salt.	Sp. gr.	Temperature.	Percentage of dissolved salt.	Sp. gr.	Temperature.
1	1.0056	14.6°	6	1.0313	15.2°
2	1.0112	16.3	7	1.0366	14.3
3	1.0161	13.7	8	1.0418	14.5
4	1.0215	13.1	9	1.0469	15
5	1.0260	14.2	10	1.0517	14.8

When uranyl chloride is heated in dry air, it is decomposed into chlorine and the dioxide, UO_2 , which is oxidised to the higher oxides, UO_3 and U_3O_8 , and is similarly decomposed when heated with

calcium hydroxide or calcium oxide, the final products being calcium uranate or a mixture of calcium uranate and diuranate [pyrouranate?], and similar results were obtained with barium or strontium oxides or hydroxides. By the action of fused potassium or sodium hydroxide, uranyl chloride is converted into a mixture of the alkali chloride and diuranate [pyrouranate?] together with a little alkali uranate; the alkali diuranates [pyrouranates?] are insoluble in water, but soluble in dilute nitric acid. By the action of sulphuric, nitric, or selenic acid, uranyl chloride yields uranyl sulphate, nitrate, or selenite respectively, and it is reduced to uranous oxide, UO_2 , by the action of hydrogen, hydrogen sulphide, zinc dust, or iron filings at a high temperature. A neutral aqueous solution of uranyl chloride gives the following qualitative reactions: with potassium hydroxide, an orange precipitate; with ammonia or methylamine, a yellow precipitate insoluble in excess of the reagent; with sodium hydrogen carbonate, an evolution of carbon dioxide and no precipitate; with potassium or sodium carbonate or sodium phosphate or potassium cyanide, a yellow, gelatinous precipitate insoluble in excess of the reagent; with ammonium sulphide, a brown precipitate becoming red; with hydrogen sulphide, a slight brown precipitate after 24 hours; with potassium ferrocyanide or ferricyanide, a deep reddish-brown precipitate insoluble in excess of the reagent.

M. A. W.

Tin Amalgams. WILLEM J. VAN HETEREN (*Zeit. anorg. Chem.*, 1904, 42, 129—173).—In the liquid state, tin and mercury are miscible in every proportion.

The points at which such mixtures solidify rise from tin to mercury and form two curves, the first from 231.6° to -34.5° for concentrations of 100—0.3 atomic percentage of tin, the second from -34.5° to -38.6° for concentrations of 0.3—0 atomic percentage of tin.

The first curve is almost a straight line until 120° , when it gradually bends till 40° is reached, at which point it falls almost perpendicularly along the temperature axis. Consequently at low temperatures the amount of tin in the saturated liquid amalgams is exceedingly small. From the liquid amalgams, represented by this curve, either pure tin separates or tin with very little mercury. The solid phase at 25° contained 94 per cent. of tin as determined analytically and 99 per cent. as determined by electrical means.

The potential differences of amalgams of from 0.001 to 100 per cent. of tin were measured at 25° against an amalgam with 15.95 per cent. With the liquid amalgams, the potential difference increases rapidly the higher the amount of tin until the saturation point with 1.2 per cent. of tin is reached. Contrasted with pure tin, the difference is about 0.5 millivolt more. By comparison of the potential differences at 25° and 50° respectively, the deduction is made that at 25° the conversion of 1 gram atom of tin into liquid amalgam with 0.01 to 1.00 atomic percentage of tin, that is, almost pure mercury, involves an amount of heat equal to about 3000 calories.

Amalgams containing 0.3 to 85 atomic percentage of tin exhibit at -34.5° a transformation which, with the addition of heat, is accompanied by contraction. A new solid phase results, mixed crystals being

probably produced where the tin may be supposed to exist in a form unknown in the free state. Between -34.5° and -38.6° those mixed crystals separate and an expansion occurs, which decreases when the percentage of tin is considerable and disappears with an atomic percentage of 60 to 70 of tin.

All amalgams up to 60 per cent. of tin solidify at -38.6° .

A. McK.

Stannichlorides of the Types $M_2'SnCl_6$ and $M'SnCl_6$. II. EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 933—947. Compare Abstr., 1904, ii, 567).—On repeating the experiments of Engel (Abstr., 1897, ii, 376; 1898, ii, 29, 119), the author obtains tin meta- and para-chlorides having properties identical with the products obtained by Engel. The meta-chloride differs slightly in composition from that prepared by this author.

From the results obtained, together with those of other investigators, the following conclusions are drawn. When α -stannic acid undergoes change, it yields an uninterrupted series of varieties of β -stannic acid, differing as regards their degree of condensation, which becomes greater as the temperature rises. The action of hydrochloric acid on these various β -stannic acids gives rise to oxychlorides which have an indefinite composition and contain a larger or smaller proportion of chlorine according as the condensation of the β -acid is small or great. The oxychlorides, differing considerably in composition, exhibit differences in properties similar to those shown by the tin meta- and para-chlorides of Engel. The reverse reactions, by which the oxychlorides are converted into a derivative of the α -acid, namely, stannic chloride, proceed the more readily the less the condensation.

T. H. P.

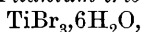
Stannates. ITALO BELLUCCI and N. PARRAVANO (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 339—346. Compare Abstr., 1904, ii, 823).—*Lead stannate*, $PbSn(OH)_6$, is obtained as a white, amorphous precipitate and loses $3H_2O$ on heating to redness. The *barium* ($+4H_2O$), *calcium*, and *strontium* salts were also prepared and analysed. All these salts are of the type $X'Sn(OH)_6$, and contain a far more stable complex than the stannichlorides (see Abstr., 1904, ii, 822). This greater stability of the stannates is borne out by conductivity measurements of solutions of potassium stannate.

T. H. P.

Titanium. I. Hydrates of Titanium Trihaloids. ARTHUR STÄHLER (*Ber.*, 1904, **37**, 4405—4410).—The author was unable to obtain the green compound, $TiCl_3 \cdot 4H_2O$, described by Glatzel (this Journal, 1877, i, 688).

Titanium trichloride hexahydrate, $TiCl_3 \cdot 6H_2O$, prepared by the electrolytic reduction of the tetrachloride, is violet. *Titanium rubidium chloride*, $TiCl_3 \cdot 2RbCl \cdot H_2O$, prepared by passing hydrogen chloride into an aqueous solution of a mixture of rubidium and titanium chlorides, which was heated on the water-bath, is green and

forms a violet solution with water. *Titanium caesium chloride*, $\text{TiCl}_3 \cdot 2\text{CsCl} \cdot \text{H}_2\text{O}$, is green. *Titanium tribromide hexahydrate*,



prepared by the electrolytic reduction of titanium tetrabromide, is violet and more unstable than the corresponding chloride. *Titanium tri-iodide hexahydrate*, $\text{TiI}_3 \cdot 6\text{H}_2\text{O}$, prepared by the electrolytic reduction of titanium tetraiodide, is violet and very unstable. A. McK.

Zirconium Salts. Constitution of Normal Zirconium Sulphate. RUDOLF RUER (*Zeit. anorg. Chem.*, 1904, 42, 87—99).—Normal zirconium sulphate does not give the characteristic reactions with oxalic acid and ammonium oxalate respectively such as the chloride gives. These reactions do not take place with solutions of zirconium oxychloride to which normal ammonium sulphate or sodium sulphate is added. The conclusion is drawn, accordingly, that zirconium sulphate in aqueous solution is constitutionally different from zirconium chloride or nitrate; its behaviour in aqueous solution is best expressed by formulating it as $\text{ZrOSO}_4 \cdot \text{H}_2\text{SO}_4$. Since this compound is represented as a dibasic acid, it forms sodium and ammonium salts of the type $\text{ZrOSO}_4 \cdot \text{SO}_4 \text{M}_2$, the complete electrolytic dissociation of which is represented by $\text{ZrOSO}_4 \cdot \text{M}_2\text{SO}_4 = \text{ZrOSO}_4 \cdot \text{SO}_4'' + 2\text{M}''$, zirconium being present in the complex anion.

The constitution of crystalline zirconium sulphate is very probably $\text{Zr}(\text{OSO}_4 \cdot \text{H}_2\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$, and not $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$.

Complex formation with concentrated solutions of sodium salts, such as sodium chloride and sodium nitrate, was also noted. In such complex salts, the zirconium is present in the cathion.

Zirconium oxychloride in aqueous solution is gradually decomposed when left at the ordinary temperature or when heated. A. McK.

Red Derivatives of Hydrated Vanadium Trichloride. ARTHUR STÄHLER (*Ber.*, 1904, 37, 4411—4412).—*Vanadium rubidium chloride*, $\text{VdCl}_5 \cdot \text{Rb}_2 \cdot \text{H}_2\text{O}$, prepared by evaporating a solution of hydrated vanadium chloride saturated with hydrogen chloride, forms a red, crystalline powder which is sparingly soluble in water. Similar *ammonium*, *potassium*, and *caesium* compounds were obtained; the *magnesium* compound has the composition $\text{VdCl}_5 \cdot \text{Mg} \cdot \text{H}_2\text{O}$. These substances are probably analogous to the chromium derivative $\text{CrCl}_5(\text{OH}_2) \cdot \text{Rb}_2$ (Werner and Gubser, *Abstr.*, 1901, ii, 453).

W. A. D.

Purification of Sodium Vanadate Liquors; the Processes of Double Decomposition for the Industrial Separation of Metals. H. HERRENSCHMIDT (*Compt. rend.*, 1904, 139, 862—864).—In the separation of vanadic acid from the mixture of sodium vanadate and silicate (compare *Abstr.*, 1904, ii, 824), the use of sulphuric acid is to be avoided as it necessitates a concentration of the liquors, introduces a third substance, namely, sodium sulphate, which has to be removed, and precipitates the vanadic acid with the silica, whereas the addition of a slight excess of vanadic acid to the dilute

solution of sodium vanadate and silicate causes the complete precipitation of the silica, the vanadic acid remaining in solution.

In all cases of separation of metals, the author recommends the use as a reagent of a compound of one of the metals already present; thus the separation of iron from manganese is effected by the carbonate or sesquioxide of manganese according to the state of oxidation of the metals in solution.

M. A. W.

Preparation of Aurous Iodide by the Action of Iodine on Gold. FERNAND MEYER (*Compt. rend.*, 1904, 139, 733—736).—Pure dry iodine has no action on gold at the ordinary temperature, but combines with it to form green, amorphous aurous iodide, AuI , at temperatures between 50° and the melting point of iodine; at higher temperatures, the iodide is obtained in the form of lemon-yellow, crystalline plates, but the reaction is reversible, and at 190° the iodide is completely decomposed into iodine and gold. In order to free aurous iodide from uncombined iodine, it is heated at 30° , whereby the latter is volatilised, it being impossible to employ any solvent for this purpose, as alcohol, ether, chloroform, or benzene decomposes the iodide. In the presence of water in a closed vessel, iodine reacts with gold to form aurous iodide provided the iodine is in excess.

M. A. W.

Volatilisation of Platinum. GEORGE A. HULETT and H. W. BERGER (*J. Amer. Chem. Soc.*, 1904, 26, 1512—1515).—An account is given of a series of experiments carried out with the object of determining the conditions under which platinum is volatilised. A large sheet of platinum foil was heated by means of an electric furnace and the loss in weight determined at intervals. In order to ascertain whether the volatilisation was influenced by the impurities present, some experiments were made with a specimen of platinum of a high degree of purity; the results showed that the pure platinum behaved in the same way as the foil.

Platinum begins to volatilise in air at a temperature of about 800° and the rate of loss increases rapidly as the temperature rises. No volatilisation occurs when the metal is heated in the absence of oxygen, and it is suggested, therefore, that at high temperatures the platinum is converted into a volatile oxide which undergoes decomposition at temperatures below 800° .

E. G.

Absorption of Hydrogen by Rhodium. L. QUENNESSEN (*Compt. rend.*, 1904, 139, 795—796).—Wilm's statement (*Abstr.*, 1881, 514) that hydrogen is more readily absorbed by rhodium than by palladium is contradicted. Rhodium was purified by heating it with sodium chloride in a current of chlorine, dissolving the product in water, converting into sodium rhodium nitrite, and crystallising the latter. The metal regenerated from this does not absorb a measurable amount of hydrogen when heated and cooled in a current of the gas. It acts as a catalyser in promoting the union of hydrogen and oxygen.

H. M. D.

Iridium Sesquisulphate and its Alums. LUIGI MARINO (*Zeit. anorg. Chem.*, 1904, **42**, 213—224. Compare Abstr., 1903, ii, 376).—Iridium sesquisulphate, $\text{Ir}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, is prepared by crystallisation from a solution of the hydrated sesquioxide in dilute sulphuric acid in the absence of air.

Iridium caesium alum, $\text{Ir}_2(\text{SO}_4)_3 \cdot \text{Cs}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, separates in regular octahedra, crystallographic measurements of which are quoted. Its aqueous solution is yellow and becomes pink when warmed above 40° . It melts at $109\text{--}110^\circ$ to a yellowish-red liquid.

Iridium rubidium alum (*loc. cit.*) is less soluble than the caesium alum; it melts at $108\text{--}109^\circ$ to a yellowish-red liquid.

Iridium potassium alum, $\text{Ir}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, forms yellow octahedra and melts at $102\text{--}103^\circ$.

Iridium ammonium alum, $\text{Ir}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, forms yellowish-red octahedra and melts at $105\text{--}106^\circ$ to a reddish-violet liquid. When it is heated at a red heat, iridium is formed.

Iridium thallium alum, $\text{Ir}_2(\text{SO}_4)_3 \cdot \text{Tl}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, forms golden-yellow octahedra.
A. McK.

Mineralogical Chemistry.

Origin of Naphtha. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1091—1096).—The author discusses the bearing of the results of Rakusin (Abstr., 1904, i, 641) on the “organic” and “inorganic” theories of the origin of naphtha (see also Charitschkoff, Abstr., 1904, ii, 180). He gives also analyses of gases evolved from the marshy volcanoes of the Caucasus. T. H. P.

Investigation of the Cañon Diablo Meteorite. HENRI MOISSAN (*Compt. rend.*, 1904, **139**, 773—780. Compare Abstr., 1893, ii, 288).—A block of the meteoric iron weighing 183 kilograms was cut through. Whilst one half of the section (area = 625 cm.²) appeared to be homogeneous and had the colour and brilliancy of iron, the other half revealed the presence of five large elliptical nodules and three smaller ones. The nodules are of a grey or black colour and extremely hard; under the microscope, they have a markedly crystalline appearance. Analyses of (I) the matrix, (II) the nodules, gave:

	Fe.	Ni.	Co.	Mg.	S.	P.	Si.	C.	Insol. in hot HCl.
I.	95.37	3.945	—	—	trace	0.144	trace	not det.	0.260
II. {	66.95	1.93	trace	trace	22.15	2.37	trace	1.96	—
	67.51	1.77	—	trace	19.91	2.30	trace	—	—

From the residue insoluble in hydrochloric acid, crystals of iron phosphide, Fe_3P_2 , have been separated. Amorphous carbon, graphite, diamond (black and transparent), and carbon silicide were also found in this residue.

The authors suggest that the nodules were originally nodules of cementite which have been acted on at a later period by the sulphur with separation of carbon. According to Le Chatelier and Ziegler's experiments, sulphide of iron can diffuse readily through masses of iron.

H. M. D.

Physiological Chemistry.

Micro-respirometric Investigations. TORSTEN THUNBERG (*Centr. Physiol.*, 1904, 18, 553—556).—The question whether nerves participate in respiratory activity has been answered in the affirmative by Baeyer, Fröhlich, and others, in confirmation of Waller's long-expressed opinion (which, however, is not quoted) that carbon dioxide is produced during the activity of nerve fibres. By means of an apparatus termed the "micro-respirometer," previously described in a Swedish publication (*Upsala Läk. s. Förh.*, 1902—1904), the respiratory exchanges in small objects like nerves can be actually measured. A number of results are given, as also are some in which the exchanges in small animals like snails were estimated. W. D. H.

Excretion of Carbon Dioxide during Exercise. GEORGE O. HIGLEY and W. P. BOWEN (*Amer. J. Physiol.*, 1904, 12, 311—335).—An instrument called the chemograph is described for obtaining a graphic record of carbon dioxide excretion in man. At the beginning of work (bicycling), the amount excreted rises after a latent period of about 20 seconds; the maximum is reached in about 2 minutes; if the work remains uniform, the output of carbon dioxide then remains uniform also, and on the cessation of work there is a latent period again of about 20 seconds, followed by a fall to the normal in about 2 minutes. There is apparently no connection between carbon dioxide production and the secondary rise of pulse rate which occurs. W. D. H.

Passage of Food-stuffs from the Stomach and through the Small Intestine. W. B. CANNON (*Amer. J. Physiol.*, 1904, 12, 387—418).—A continuation and amplification of the author's previous work by means of the Röntgen rays; the method is capable of yielding data on the rate of peristalsis and of segmentation into masses. This is most rapid with carbohydrate food. Carbohydrates reach the large intestine in 4, fats in 5, and proteids in 6 hours. Data are also given when these different kinds of food are mixed or administered in succession. The animals used were cats. W. D. H.

Influence of Surgical Operations on Carbohydrate Metabolism. EDUARD PFLÜGER, BERNHARD SCHÖNDORFF, and FRIEDRICH WENZEL (*Pflüger's Archiv*, 1904, 105, 121—176).—Gly-

cosuria is often described as a common sequel to surgical operations. The grounds for this opinion are not regarded as satisfactory; the urine may contain a reducing substance, but this is not necessarily sugar. A discussion follows (largely polemical) concerning the best tests for sugar in urine. Even the fermentation test is untrustworthy. Most reliance should be placed on the polarimetric test and Worm-Müller's modification of the copper test. From the examination of some hundreds of urines, the conclusion is drawn that many forms of so-called transitory glycosuria (including those produced surgically and by anæsthesia) do not exist.

W. D. H.

The Behaviour of Carbohydrates in Autolysis. CARL NEUBERG and RICHARD MILCHNER (*Chem. Centr.*, 1904, ii, 1422; from *Berlin klin. Woch.*, 41, 1081—1084).—In autolysis of the liver, the proteid matter of which contains 3·6 per cent. of glucosamine, no hydrolysis of the latter takes place with the liberation of a unimolecular sugar. On the other hand, in autolysis of the pancreas, *l*-xylose is liberated from the nucleo-proteid; in this, autolysis differs from tryptic digestion. It is believed that the pentose group is united not to the proteid molecule, as is the glucosamine of liver proteid, but to the nucleic acid of the pancreatic proteid (guanylic acid) after the manner of a glucoside, and this will explain the difference seen in autolysis. The nitrogen-free "transport sugar" of blood globulin (Langstein) is also probably combined as in a glucoside.

W. D. H.

Utilisation of Proteids without the Intervention of Digestion. LAFAYETTE B. MENDEL and ELBERT W. ROCKWOOD (*Amer. J. Physiol.*, 1904, 12, 336—352).—Recent research tends to show that during digestion proteolysis is more profound than was formerly considered to be the case, and that the tissue proteids are reconstructed from the simple decomposition products. Experiments were therefore undertaken to study the fate of proteids introduced directly into the blood stream or into the peritoneal cavity. Edestin (from hemp seed) and excelsin (from Brazil nuts) were introduced slowly, and were apparently retained for the most part. At any rate, they were not discovered in the urine or bile. Rapid injection causes toxic symptoms, especially inhibition of heart and respiration. The urine contained a proteose-like substance after injection of excelsin, but not of edestin. If edestin or casein is introduced into a loop of intestine from which digestion processes are excluded, they are not absorbed, but their proteoses and peptones rapidly disappear.

W. D. H.

Inanition Studies. III. In Libella. IV. In Bees. B. SLOWTZOFF (*Beitr. Chem. physiol. Path.*, 1904, 6, 163—169, 170—174).—A continuation of the author's work on inanition on the lines of his previous researches.

W. D. H.

Further Proof of Ionic Action in Physiological Processes. C. HUGH NEILSON and ORVILLE H. BROWN (*Amer. J. Physiol.*, 1904, 12, 374—386).—Non-electrolytes have no effect, except in solutions of 1 mol. concentration or more, on the decomposition of hydrogen per-

oxide by platinum black or by an aqueous extract of kidney; in concentrations greater than 1 mol., there is an inhibitory effect, which increases with the concentration. A salt in dilute concentration exerts either a depressing or stimulating effect, the former depending on the positive, the latter on the negative ion. W. D. H.

Action of Salts on Muscle and Nerve. ERNST OVERTON (*Pflüger's Archiv*, 1904, 105, 176—290).—The experiments were mainly made with thin muscles, like the frog's sartorius. Solutions of potassium chloride isotonic with blood kill the muscles in a few minutes and cause them to increase in weight. In a mixed solution of the chlorides of sodium and potassium, the muscle remains almost impermeable to potassium chloride until it is injured by that salt. Other potassium haloids and potassium nitrate behave in the same way. Loss of indirect excitability occurs rapidly when quite a small percentage (0.06 to 0.07) of potassium chloride is added to a sodium chloride solution; this effect is removed by the addition of calcium chloride or by placing the preparation in Ringer's solution (confirmatory of Locke). The harmful action attributed to potassium ions is like that caused by curare. Rubidium, caesium, and ammonium salts act like potassium, with some differences of detail which are fully described. Strontium acts like calcium as an antagonist to these, but barium and magnesium salts do not. It cannot, therefore, as Loeb supposes, be a simple question of valency of ions. W. D. H.

Biological Importance of Iron. ALESSANDRO BALDONI (*Chem. Centr.*, 1904, ii, 1476; from *Arch. exp. Path. Pharm.*, 52, 61—68).—Iron in nutriment is not only of importance in hæmoglobin formation, for all the tissues contain iron. The blood-free epidermis, the crystalline lens, the tissues of the crayfish, and, among plants, Iceland moss were investigated, and all were found to contain small amounts of iron. W. D. H.

Influence of Local Temperature on Glycolysis in the Capillaries. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1904, 139, 622—625).—After section of the sciatic nerves in dogs, one leg was immersed in cold water, the other in warm water. Ten minutes later, blood was withdrawn from the carotid artery and both crural veins. The venous blood contained less sugar than the arterial, but the loss was greatest in the venous blood of the cooled limb. Exceptions to the rule were noticed, but the total number of experiments performed is not recorded. If the blood is collected and kept, glycolysis occurs most rapidly in the blood where it occurred most rapidly *in vivo*. W. D. H.

Formation of Aromatic Fatty Acids in the Animal Body. FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1904, 6, 150—162).—A study of the metabolism of fatty compounds in especial relationship to the origin in the body of those containing an aromatic nucleus. A large number were administered to animals; some were excreted un-

changed, others were oxidised in various ways, whilst in others the amino-group was removed. W. D. H.

Production of Choline from Lecithin and Brain Tissue. ISIDOR H. CORIAT (*Amer. J. Physiol.*, 1904, 12, 353—364).—In view of the work of Mott and Halliburton on the importance of recognising choline as a sign of breakdown of nervous tissues, the theory is advanced that the splitting off of choline from lecithin is due to ferment action, but attempts to isolate the enzyme were unsuccessful. The enzyme is destroyed by heating, and acts best in slightly alkaline media. It comes into play during autolysis, but the yield of choline is small. During putrefaction, the yield is larger. Pepsin and trypsin fail to act on the lecithin of brain tissue, and inhibit autolysis. Lipase, however, is capable of splitting lecithin. Of the methods tried, heating lecithin with barium hydroxide was the only one which led to a theoretical yield of choline. W. D. H.

Receptivity of Cells in Normal and Immunised Animals. MARTIN JACOBY (*Beitr. chem. Physiol. Path.*, 1904, 6, 113—131).—A contribution to the study of immunity in its various stages, with theoretical deduction on its mechanism. Some of the more important results are as follows: the receptor groups in the blood corpuscles for ricin are fixed there firmly, and cannot be removed by washing, by great pressure, or by digestive ferments. After blood corpuscles are treated with eel serum, the toxicity of the latter poison is diminished; in some cases it is increased: this is explained by the presence of a mixture of toxoids and toxins, the former being taken up by the corpuscles first. At 0°, rabbits' corpuscles are only agglutinated by eel serum; at 35°, they are completely hæmolyzed. Varieties of corpuscles which are not very susceptible to a toxin have their susceptibility increased during the progress of immunisation. W. D. H.

The Individuality of Trypsin. LEO POLLAK (*Beitr. chem. Physiol. Path.*, 1904, 6, 95—112).—That trypsin is not a single substance has been stated by Vernon and others. It is regarded as possible that the pancreatic enzyme really consists of a number of specific ferments each acting on different proteids. In support of this, it is shown that treatment of a pancreatic extract with acid destroys its power of digesting serum, egg-white, and fibrin, but not of digesting gelatin. The latter property is therefore ascribed to a specific ferment, *glutininase*. Attempts by fractional methods to obtain a ferment acting only on serum proteids were unsuccessful, but led to the discovery of an *anti-glutininase*. This is not dialysable, but is not a ferment, not being destroyed by boiling. It is not identical with the anti-trypsin of blood serum. W. D. H.

Hæmolysinogenic and Agglutininogenic Action of Laked Corpuscles. GEORGE N. STEWART (*Amer. J. Physiol.*, 1904, 12, 363—373).—Further experiments in support of the author's earlier conclusion that the stromata and liquid of water-laked corpuscles cause the production of sera with specific hæmolytic and agglutinating power.

The latter is the more marked effect, as is also the case with the serum obtained after the injection of stromata laked by freezing and thawing. Filtration through porous earthenware removes the agglutininogens and hæmolysinogens from the liquid of corpuscles laked by freezing and thawing and by foreign serum.

W. D. H.

Action of Radium Emanations on Chymosin. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1904, 6, 175—176).—Even long exposure to radium emanations causes no marked deterioration in the activity of chymosin (rennin).

W. D. H.

Anti-substances against Croton in the Normal Organism. FRANZ ALEXANDER LUST (*Beitr. chem. Physiol. Path.*, 1904, 6, 132—149).—The anti-substance found in the pig's gastric mucous membrane is resistant to heat, and is active in neutral, weakly acid, or weakly alkaline media. It is precipitable by alcohol or ether, or by saturation with ammonium sulphate. It is not dialysable and is not destroyed by artificial gastric digestion. It does not give the biuret reaction or any reaction with iodine-potassium iodide solution. It is not present in other organs, except in small quantities in those like the lungs and liver, which are rich in blood. Various animals differ a good deal in their susceptibility to croton.

W. D. H.

Urinary Indoxyl. LÉON GRIMBERT (*J. Pharm. Chim.*, 1904, [vi], 20, 398—407).—Human urine always contains indoxyl; its presence is not pathological; the amount varies with food, work, fatigue, and intestinal disorders. Even large quantities have no necessary importance; there is no ground for supposing it to be due to liver disease. Scatoxyl pigments do not occur in the urine, for by oxidation in the body scatole loses its methyl group and is converted into indoxyl. Red colours attributed to scatoxyl are produced by indirubin.

W. D. H.

Studies in Diuresis. X. The Situation in the Kidney where Foreign Substances are Excreted. JOH. BIBERFELD (*Pflüger's Archiv*, 1904, 105, 308—320).—The experiments were made with pigments, especially Berlin-blue, and they lead to the conclusion that this substance is excreted by the convoluted tubules. This work confirms in the main von Soberieranski's recent researches with indigo-carmin; a few points of difference are discussed. Some of the observations throw doubt on Ludwig's doctrine of reabsorption of water in the tubules.

W. D. H.

A Case of Leucæmia. F. PARKES WEBER (*Trans. Pathol. Soc. London*, 1904, 55, 288—296).—A case is described in which some resemblances to pernicious anæmia are noted; but there was no abnormal amount of urinary pigment, and no reaction for "free iron" in spleen, liver, and kidneys. There was great hyperplasia of the spleen and prevertebral hæmolymp glands, but not of the lymphatic glands proper. The bone marrow was abnormally firm, and contained excess of connective tissue.

W. D. H.

Pseudo-lipæmia. JOHN FAWCETT and A. E. BOYCOTT (*Trans. Pathol. Soc. London*, 1904, 55, 332—336).—In a fatal case of sarcoma of the pancreas, the blood-plasma was creamy, but prolonged centrifugalisation produced hardly any change. The creamy appearance is due to extremely minute particles of irregular shape, which are insoluble in ether or in 1 per cent. acetic acid. They are stained blue by Jenner's stain, but give no reaction for fat with osmic acid or Soudan III. The amount of fat in the blood was only 0.38 per cent., a number which comes within normal limits. The blood corpuscles showed nothing noteworthy. The creamy appearance is attributed, as in some cases recorded by others, to proteid material. W. D. H.

The Action of Alcohols on Echinoderm Eggs. HERMANN FÜHNER (*Chem. Centr.*, 1904, ii, 1517—1518; from *Arch. exp. Path. Pharm.*, 52, 69—82).—A large series of alcohols was investigated, and the general conclusion drawn that each successive member of a series is more toxic towards the eggs than the preceding. The secondary alcohols are less active. Urethane is about twice as poisonous as *n*-propyl alcohol, and about the same as *n*-butyl alcohol. Chloral hydrate approaches octyl alcohol in toxicity, and is 90 times more poisonous than urethane. Urea has no action. Glycerol, mannitol, and sucrose cause greater harm than can be explained by osmotic phenomena. Mixtures of alcohol with colloids, multivalent alcohols with urea and with sugar, are more toxic than the alcohols alone. Injurious effects in the more advanced larvæ are also described. W. D. H.

The Action of Cobalt, Rhodium, and Chromium-ammonium Compounds on the Animal Organism. JOHANNES BOCK (*Chem. Centr.*, 1904, ii, 1515—1517; from *Arch. exp. Path. Pharm.*, 52, 1—29, 30—38).—Hexaminecobalt chloride is strongly toxic, its most marked action being like that of curare. Aquopentamminecobalt sulphate acts similarly, but is not so toxic. Diaquotetramminecobalt sulphate is 100 times less poisonous. A number of other similar compounds were also investigated. A comparison of the lethal doses in frogs and mammals shows that the amount of cobalt present makes no difference, but the toxic action depends on the number of ammonium and H_2O groups, and on the nature of the acid residues in the complex radicles. The corresponding compounds of rhodium and chromium gave analogous results.

Non-toxic doses of hexaminecobalt chloride cause in frogs fascicular clonic contractions, which are due to excitation of motor nerve bundles. W. D. H.

Toxicity of Amylene $\alpha\beta$ -Chlorohydrin. L. LAUNOY (*Compt. rend.*, 1904, 139, 650—652. Compare *Abstr.*, 1904, ii, 501).—The toxic action of this substance was tested on the dog, rabbit, mouse, guinea-pig, fowl, and pigeon. The above order is that of decreasing receptivity; that is, the animal most easily killed is placed first. *In vitro*, amylenic chlorohydrin has a globulicidal action, which is not exercised *in vivo*. W. D. H.

Toxins and Antitoxins. Diphtheria Poison. SVANTE ARRHENIUS and THORVALD MADSEN (*Chem. Centr.*, 1904, ii, 1420; from *Bull. acad. roy. Danemark*, 1904, No. 4).—This contribution to immunity is largely polemical against Ehrlich. No foundation is discovered for the existence of prototoxoids or toxones. The dissociation constant varies but little. The diphtheria toxin is regarded as a homogeneous substance, and behaves like a unimolecular material. The loss of activity it undergoes is attributed to its gradual conversion into an atoxic substance or toxoid. The toxin and its toxoid react in equivalent quantities with the same amount of antitoxin, both products called *toxinan* and *toxoidan* respectively being non-poisonous.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Epidemic or Bacillary Dysentery. R. H. FIRTH (*Trans. Pathol. Soc. London*, 1904, **55**, 340—375).—Two types of bacilli are obtainable from dysenteric excreta: one, non-pathogenic, is able to decompose maltose, galactose, and mannitol with the formation of acid, but not of gas, and also able to produce indole; the other, which is pathogenic and to which the term *Bacillus dysenteriae* should be restricted, does not possess these characters. The former may be a degraded or transitional form of the latter, but this is uncertain, as also is their relationship, if any, to the bacilli of enteric fever. The prospects of establishing an acquired immunity against bacillary dysentery are not encouraging; experiments on rabbits and guinea-pigs show that passive immunity is brief, although active immunity is of longer duration. W. D. H.

Development of Organic Matter in Seeds during Maturation. GUSTAV ANDRÉ (*Compt. rend.*, 1904, **139**, 805—807).—In the maturation of lupin and haricot seeds, the percentage amount of ash was always greater at the commencement than at the end. The same was observed as regards total nitrogen except in the case of lupins. The non-nitrogenous organic matter is at first in the form of soluble carbohydrates. N. H. J. M.

Desiccation of Plants and Vegetable Tissues. Period of Maturation not Reversible. Final Equilibrium in Average Atmospheric Conditions. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, **139**, 693—702).—The water retained by plants at the ordinary temperature, under given conditions of temperature and atmospheric moisture, corresponds with an equilibrium or limit. This limit varies much less for a given interval than the temperature of the air or the vapour tension of the air, provided that extremes are avoided.

N. H. J. M.

Absolute Desiccation of Plants and Vegetable Substances : Period of Artificial Desiccation. Reversibility by Atmospheric Moisture. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 702—716).—The results of experiments with different plants established the reversibility between evaporation, in perfectly dry air, of the water retained in ordinary air and the absorption of aqueous vapour in ordinary air by plants dried by heating at 110°. The amount of water fixed by a dried plant is generally less than the amount necessary to a live plant. The reciprocity is therefore independent of vital action. N. H. J. M.

Desiccation of Plants. Period of Vitality. Humectation by Liquid Water. Reversibility Imperfect. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 761—773).—Experiments on the absorption and exhalation of water by plants are described. N. H. J. M.

Importance of Calcium and Magnesium Salts for Plants. FR. GÖSSEL (*Chem. Centr.*, 1904, ii, 1157 ; from *Verh. Ges. Deut. Ntf. Aerzte*, 1903, ii, 101—104).—The results of water- and soil-culture experiments failed to confirm Loew's theory that there must be a certain relation of CaO : MgO. In water cultures, the highest yields of barley and beans were obtained when CaO : MgO = 0·4 : 1, instead of 1 : 1 for barley and 3 : 1 for beans as Loew states. The conclusion is drawn that a definite relation between the two bases is unnecessary, and that the effect of lime depends especially on the character of the soil. N. H. J. M.

Organic Compounds of Metals in Plants. CHARLES F. SCHLAGDENHAUFFEN and E. REEB (*Compt. rend.*, 1904, 139, 980—983).—The residue obtained after incinerating the light petroleum extract of ripe barley consists of phosphoric acid and the phosphates of sodium, calcium, manganese, and iron, which existed in the plant as the distearyl-glycerophosphate of neurine and the metallic derivatives of other lecithins respectively (compare *Abstr.*, 1902, ii, 625). The residue, similarly obtained from oats, rye, and wheat, contained potassium instead of sodium. M. A. W.

Evolution of the Weight and the Organic Matters of Leaves during Necrobiosis in White Light. L. BEULAYGUE (*Compt. rend.*, 1904, 139, 814—816).—Analyses are given of leaves of *Bougainvillea spectabilis* which had been dried at 110° immediately after being detached, and of similar leaves allowed to die gradually in boxes of colourless, red, yellow, green, and blue glass. These analyses were first made on the second day and again at intervals of two days. The leaves were well mixed every day. In the present paper, the results obtained with colourless glass are discussed.

The total carbohydrates (in 100 leaves) diminished gradually from 2·566 grams on the second day to 2·400 grams on the twelfth. The sugar diminished slightly to the sixth day, then slightly increased. The non-digestible proteid nitrogen and the nitrogen as nuclein increased regularly from 0·195 to 0·287 gram and from 0·182 to 0·273

gram respectively. The nitrogen as amides was almost exactly the same on the twelfth day as on the second day, but somewhat irregular results were obtained on the intermediate days. The results relating to total and to digestible proteids also show irregularities.

N. H. J. M.

Non-proteid Nitrogenous Constituents of Agricultural Plants. ERNST SCHULZE (*J. Landw.*, 1904, 52, 305—336).—The amount of non-proteid in seeds varies considerably; it is highest in leguminous and lowest in cereal and oily seeds. Choline was found in all the seeds examined; betaine was found in vetches, sunflower, and wheat; trigonelline in peas, hemp, and oats.

Etiolated seedlings contain either asparagine or glutamine; if both occur in the same plant, the amount of the one greatly predominates over that of the other. Leguminous seedlings, cereals and grasses, and poppy contain asparagine, whilst glutamine is found in pumpkins, ricinus, sunflower, white mustard, rape, cress, and radish, &c. Glutamine is, however, much less abundant than asparagine, the maximum amount in these plants being 2.5 per cent. in the dry matter. More than 25 per cent. of asparagine is sometimes found. Etiolated plants also contain the hexone bases, aminovaleric acid, leucine, phenyl-alanine, and tyrosine. Nuclein bases occur only in small amounts.

Roots and tubers resemble etiolated seedlings as regards their nitrogenous constituents. Asparagine or glutamine is nearly always the most abundant amide. Asparagine occurs in potatoes, glutamine in sugar beet and mangolds. Tyrosine was obtained from potatoes and mangolds, leucine, arginine, lysine, and histidine from potatoes. Sugar beet contains, besides glutamine, asparagine, leucine, tyrosine, betaine, arginine, guanidine, nuclein-bases, carnine, allantoin, choline, vernin, and ricine. The green parts of plants contain a considerable number of amides, but the amount actually separated was small.

As regards food value, it is probable that amides are more like proteids than carbohydrates, as stated by Lehmann. N. H. J. M.

Milk of Castilloa Elastica. ANNE W. K. DE JONG (*Ber.*, 1904, 37, 4398—4399. Compare Abstr., 1904, ii, 762, 763).—The following were detected in the juice of *Castilloa elastica*: proteids, tannic acid, an acid, $(C_{17}H_{30}O_{10})_x$, potassium chloride, a sugar, and a substance, the neutral solution of which assumed a green colour on exposure to the atmosphere. A. McK.

Chemistry of Celery (*Apium Graveolens*). MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1904, 25, 1030—1034).—The aqueous extract of freshly-cut celery roots is found to contain asparagine, tyrosine, and mannitol. G. Y.

Composition of Orange Juice. K. FARNSTEINER and W. STÜBER (*Zeit. Nahr. Genussm.*, 1904, 8, 603—605).—The juices to which the following results refer were obtained from the various oranges after

the peel, spongy tissue, and seed had been removed. The expressed juice only came into contact with wooden vessels.

Grams per 100 c.c.	From oranges of unknown origin.		From	From
	Fresh.	Fermented.	Valencia oranges.	Messina oranges.
Specific gravity at 15°	1·0429	1·0084	1·0464	1·0451
„ „ after boiling	1·0454	1·0159	1·0466	1·0455
Total solids, dried 2½ hours at 100°	10·73	3·55	10·92	10·85
Citric acid (anhydrous)	1·19	1·25	1·79	1·47
Total sugars (as invert sugar)	8·26	0·38	7·65	7·86
Mineral matters (ash)	0·41	0·42	0·52	0·50
Alkalinity of ash (c.c. N/1 acid)	5·40	5·62	7·20	6·40
Nitrogen	0·064	0·053	0·099	0·075
Phosphoric acid	—	0·026	0·027	0·042
Glycerol	0·38	0·61	0·34	0·28
Alcohol	1·44*	4·29	—	—
Polarisation in 200 mm. tube, direct	—	—	- 0·11°	+ 2·45°
Polarisation in 200 mm. tube after inversion	—	—	- 3·16°	- 3·66°

W. P. S.

The Formation of Formaldehyde in the Combustion of Tobacco. AUGUSTE TRILLAT (*Compt. rend.*, 1904, 139, 742—744. Compare Abstr., 1904, i, 713).—Tobaccos from various sources were burnt in the form of cigars, cigarettes, or in clay or wooden pipes, and the formaldehyde in the products of combustion estimated as tetramethyldiaminodiphenylmethane, with the result that the quantity of formaldehyde formed varies little with the origin of the tobacco and amounts to 0·05 to 0·1 per cent. of the weight of the substance burnt; the yield was slightly higher in the case of the clay than of the wooden pipe, probably owing to surface catalytic action. The formaldehyde does not, however, exist in the free state in the products of combustion, but combines with the nitrogenous bases (such as nicotine) (compare Schindelmeister, Abstr., 1903, ii, 115) also present in the tobacco smoke to form compounds which possess none of the deleterious properties of the two constituents.

M. A. W.

Treatment of Soil with Ether, Carbon Disulphide, Chloroform, Benzene, and Hydrogen Peroxide. Effect on the Growth of Plants. FRIEDRICH NOBBE and L. RICHTER (*Landw. Versuchs-Stat.*, 1904, 60, 433—448).—Application of ether and hydrogen peroxide to soil in which peas were grown failed to sterilise it and were rather favourable to growth than unfavourable. Ether applied as an emulsion increased the produce 41·5 per cent.

* A small quantity of an alcoholic solution of salicylic acid had been added to this juice.

Further experiments in which oats were grown in soil treated with ether, benzene, carbon disulphide, and chloroform showed that higher yields were obtained in every case than with untreated soil, and that larger amounts of nitrogen and total ash were assimilated. The action extended to second crops after the odour of the substances applied had disappeared.

It is shown that the soils underwent no change. The increased results would seem to be due to a directly stimulating action of the substances employed or of their products of decomposition.

N. H. J. M.

Effect of Soil Sterilisation on Plant Development. CARL SCHULZE (*Bied. Centr.*, 1904, 33, 748—751; from *Jahresb. Ver. Vertret. ang. Bot.*, 1904).—Experiments are described in which various plants were grown in normal and in sterilised arable and meadow soils. Sterilisation was effected by heating at 100° or at 125°. The different plants showed very different degrees of sensitiveness towards the decomposition products of the soil, and the results also varied according to the nature of the original soil, sterilised meadow soil being more injurious than sterilised arable soil. Mustard proved to be particularly sensitive, whilst oats grown in sterilised arable soil showed very slight signs of injury. Plants which were able to recover from the injury due to the heating of the soil were sometimes much more luxuriant than those grown in normal soil.

Sterilisation had least injurious effect on garden soil; oats grown in the sterilised soil showed no signs of injury and the yield was raised by 30—70 per cent. Similar results were obtained with mustard.

The injurious effect of sterilisation on meadow soil is almost entirely overcome by the application of calcium carbonate. The yield of mixed grasses was raised by more than 100 per cent. by sterilising and adding calcium carbonate.

N. H. J. M.

Solubility of Soil Constituents. FELIX MACH (*Chem. Centr.*, 1904, ii, 1164—1165; from *Verh. Ges. Deut. Nf. Aerzte*, 1903, ii, 91—94).—Ferric, aluminium, and tricalcium phosphates were dissolved to some extent by water. Water containing hydrated silica only dissolved aluminium phosphate somewhat more than water alone. Water and humic acid dissolved two or three times as much, a saturated solution of carbon dioxide much less ferric and aluminium phosphates, but twice as much calcium phosphate as pure water.

Calcium and magnesium carbonates are about twice as soluble in water and silica as in water alone. The solubility of gypsum was about the same in all the solvents. Carbon dioxide somewhat increased the solubility of felspar and oligoclase and still more the solubility of the calcium of desmine and natrolite. In the case of muschelkalk and basalt, carbon dioxide increased the solubility of every constituent except sulphuric acid and silica.

N. H. J. M.

Black Soils of Legienen, Rössel, in East Prussia. EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1904, 60, 407—418).—Complete chemical analyses and mechanical separations of several samples of

surface and subsoil are given. The black soils both of East and West Prussia contain much less humus than those of Russia.

N. H. J. M.

Humic Acids of Grey Sand and Brown Sandstone. ADOLF MAYER (*Landw. Versuchs-Stat.*, 1904, 60, 475—480).—The humic acids of brown sandstone contain less carbon than those of grey sand. It is probable that the humic acids of grey sand are oxidised when ferric oxide is present, and dissolve as ferrous salts of oxyhumic acids. These are oxidised in the subsoil to insoluble ferric salts.

N. H. J. M.

Beet Molasses of Various Origin. TH. DIETRICH and FELIX MACH (*Landw. Versuchs-Stat.*, 1904, 60, 347—357).—Analyses of twenty samples of molasses. The results include dry matter, ash, total sugar, invert sugar, total nitrogen, proteid nitrogen, nitric nitrogen, carbon dioxide, lime, and alkalinity or acidity.

N. H. J. M.

Analytical Chemistry.

Modified Gas-burettes. JULIUS ZRZAWY (*Chem. Zeit.*, 1904, 28, 1172).—Hempel burettes so constructed that it is possible to read the volume of gas to 0.01 c.c. L. DE K.

A New Burette for Testing Normal Solutions. A. HESSE (*Chem. Zeit.*, 1904, 28, 1172).—The burette is fitted with a beaker-shaped cup. The first 0.5 c.c. and the last 49–51 c.c. are divided to 1/100 c.c., the tube being drawn out at these places; the remainder is divided as usual to 1/10 c.c. The parts drawn out are not calibrated. It is merely intended for checking normal solutions. L. DE K.

Determination of the Neutralisation Point by Conductivity Measurement. II. FRIEDRICH W. KÜSTER, MAX GRÜTERS, and W. GEIBEL (*Zeit. anorg. Chem.*, 1904, 42, 225–234. Compare Abstr., 1903, ii, 611).—Ten c.c. of *N*/10 sulphuric acid were diluted with 500 c.c. of water and then *N*/10 sodium hydroxide gradually added, the conductivity of the solution being measured after the addition of each c.c. of alkali. The conductivity of the sulphuric acid falls regularly as the neutralisation proceeds until a minimum value is attained exactly at the neutralisation point; an increase in the value occurs when more sodium hydroxide is added. By this method, the end-point may be determined much more sharply than by the use of any indicator.

Phosphoric acid behaves as a monobasic acid; the break of the conductivity curve coincides with the results obtained by titrating phosphoric acid with methyl-orange as indicator.

In order to show how the method may be applied when indicators fail, 20 c.c. of $N/10$ potassium dichromate were mixed with 10 c.c. $N/10$ sulphuric acid and then titrated with $N/10$ sodium hydroxide by conductivity measurement as before; the sulphuric acid present can be titrated as sharply as if the dichromate were absent. Similar measurements were made with potassium permanganate in the solution instead of potassium dichromate.

The presence of precipitates also does not impair the accuracy of the method, thus citric acid may be titrated by barium hydroxide.

When weak organic acids were titrated by the gradual addition of sodium hydroxide, the minimum of conductivity was attained too soon; the method yields correct results, however, when the acid is added to the alkali. Acetic, lactic, tartaric, and citric acids were titrated in this manner.

Determinations of the amount of acetic acid in a strongly coloured vinegar examined are quoted. The total acid in a specimen of red wine was also determined.

Magnesia and various alkaloids were similarly titrated.

A. McK.

The Theory of Indicators and its Bearing on the Analysis of Physiological Solutions by means of Volumetric Methods. GEORGE H. A. CLOWES (*Amer. J. Pharm.*, 1904, 76, 453—467, 511—525).—This paper has for its object the outlining of the nature of the various classes of indicators used in acidimetry and alkalimetry, studying their behaviour towards various weak bases and acids which may occur in the course of physiological work; further, to make a series of tests on artificial and normal stomach contents, pancreatic fluids, blood serum, &c. With regard to the behaviour of amino-acids, asparagine, glycine, leucine, tyrosine, and aspartic acid towards indicators, experiments were made in which their action was compared with that of the ammonium salts of formic, acetic, and lactic acids, acetamide, formamide, and urea. Poirrier's blue was found to be sensitive to all the free acid groups, and entirely indifferent to ammonia and amino-groups. Phenolphthalein is less sensitive to acid groups and far more sensitive to ammonia than Poirrier's blue. Alizarin is sensitive to both ammonia and strong acid groups, but is indifferent to the weak acid groups in asparagine, tyrosine, &c., and also to the amino-group of these compounds.

Phloroglucivanillin is entirely indifferent to all weak organic acids. This indicator is of great value in differentiating the weak bases, being sensitive not only to ammonia, but also to the amino-group in asparagine, glycine, leucine, and tyrosine, and indifferent to the amino-groups present in acetamide, formamide, and urea. From the experiments with proteids, &c., it seems possible that some sort of relationship obtains between the various nitrogen-containing groups in the proteid and the end-points of different indicators. The comparison of volumetric with gravimetric analyses of normal and pathological stomach contents showed that, provided a purely proteid test meal was employed, the phenolphthalein end-point indicates fairly accurately the total available hydrochloric acid present, both free and

combined more or less feebly with proteids. The actual free acid is given by phloroglucinvanillin. After allowing for the influence of phosphates and traces of organic acids, the range of titration between the end-point of phloroglucinvanillin and that of phenolphthalein may be said to be a function of the basic affinities of the proteids and their decomposition products present. Under conditions where peptic digestion fails to take its normal course, the above rules are no longer applicable. In tryptic digestion, the range of titration, after allowing for the influence of carbon dioxide, is at first more or less proportionate to the amount of proteid brought into solution, but subsequently increases in undue proportion to the total nitrogen as the digestion proceeds. The wide variation between the end-points of phenolphthalein, alizarin, and phloroglucinvanillin in estimating the alkalinity of blood serum emphasises the necessity of certain uniform standards for this purpose. With regard to urine, the titration results are fairly dependent on the amount of phosphates present. In the presence of any considerable quantity of ammonia, which exerts a more powerful effect on alizarin and phenolphthalein than urea, the urine will be less acid or even alkaline to phenolphthalein, and more strongly alkaline to alizarin than is normally the case.

W. P. S.

Standardisation of Normal Solutions. MAX SCHOLTZ (*Arch. Pharm.*, 1904, 242, 575—578).—Of an approximately 0.01*N* sodium hydroxide solution, 10 c.c. required the following volumes, I, of an approximately 0.01*N* hydrochloric acid; and of the same acid, 10 c.c. required the following amounts, II, of the same alkali; according to the indicator employed:

	Phenolphthalein.	Litmus.	Rosolic acid.	<i>p</i> -Nitrophenol.	Iodoeosin.	Methyl-orange.
I.	9.68	9.83	9.87	10.00	9.80	10.70 c.c.
II.	10.08	9.92	9.92	9.99	9.68	9.28 „

When standard solutions as weak as these are being used, it is evidently important that the indicator and the direction of the change of colour in the standardisation should be the same as are employed in the actual estimation.

The results are discussed from the point of view of the theory of electrolytic dissociation (compare *Abstr.*, 1904, ii, 771). C. F. B.

Potassium Bromide as Indicator when using Fehling's Solution. PIO BERTI (*Chem. Centr.*, 1904, ii, 1433; from *Bull. Assoc. Chim. Sucr. et Dist.*, 21, 1234—1236).—A drop of the liquid is put on to a double piece of filter paper resting on a porcelain plate, and, after removing the paper, the moist spot is touched with a particle of potassium bromide and a drop of sulphuric acid. If there should still be a trace of dissolved copper, a violet colour is noticed owing to the formation of cuprous bromide.

L. DE K.

Apparatus for Extracting Liquids with Chloroform. ERICH BAUM (*Chem. Zeit.*, 1904, 28, 1172).—A modification of the van Rijn

apparatus (Abstr., 1896, ii, 17), which consists in fixing the overflow tube (siphon) in the lower part of the extractor, thus allowing the use of solvents heavier than water.

L. DE K.

New Extractor. ANDREA SANNA (*Gazzetta*, 1904, 34, ii, 224—228).—This extractor consists of a flask fixed obliquely and filled about half-full with the substance to be extracted and the solvent. Through the double-bored stopper of the flask pass the bent inner-tube of an inverted condenser and a short glass tube furnished with a cock and an india-rubber tube. The upper end of the condenser tube is also bent and passes into an Erlenmeyer flask, through the stopper of which passes also a short glass tube with a cock. The latter is left open during the heating of the substance with the solvent. When the extraction is complete, the condenser and Erlenmeyer flask are turned round so that the end of the bent condenser tube is now at the lowest part of the round flask, whilst the Erlenmeyer flask is at a still lower level. The cock attached to the round flask is then opened and the solution forced through the condenser tube into the Erlenmeyer flask. The apparatus is then inclined so that the round flask is lower than the Erlenmeyer and the solvent distilled off from the latter into the round flask, the cock attached to the Erlenmeyer flask being meanwhile kept closed. The extracted material then remains in the Erlenmeyer flask. These operations may be repeated until the extraction is complete.

The apparatus gives good results for the extraction of liquids or solids, as, for example, in the determination of fat in cheese, butter, &c., and it acts more quickly than a Soxhlet or Garralowschy extractor. In determining fat in a material like cheese, it is advisable to pack the substance in filter paper tied up with cotton, as this prevents solid particles from being carried away.

T. H. P.

Palladium-Hydrogen as a Reducing Agent in Quantitative Analysis. ALFRED C. CHAPMAN (*Analyst*, 1904, 29, 346—357).—In an investigation undertaken for the purpose of ascertaining to what extent palladium-hydrogen could be employed as a quantitative reducing agent, it was found that ferric salts, as well as potassium ferricyanide, were completely and readily reduced. Chromates in acid solutions were reduced to chromic salts. The palladium was employed in the form of foil of such thickness that a piece 2 inches square weighed about 8 grams. A piece of thick palladium wire was welded to this, and the foil was charged by being made the negative electrode in an ordinary cell containing dilute sulphuric acid, the current being obtained from the main or from accumulators. The charged metal was, after washing, suspended in the boiling solution under examination. In the case of cupric, stannic, arsenic, manganic, vanadic, and molybdic compounds, the reduction was either incomplete or imperfect. Potassium chlorate was only partly reduced, whilst bromates and iodates were not attacked. Ceric salts were reduced to cerous salts, which latter could be titrated with ferrous ammonium sulphate solution, as the lower oxide was itself capable of oxidising the ferrous solution.

W. P. S.

Action of Hydrochloric Acid on Potassium Chlorate. A. KOLB and E. DAVIDSON (*Zeit. angew. Chem.*, 1904, 17, 1883—1887).—During the action of hydrochloric acid on potassium chlorate in the presence of potassium iodide, atmospheric oxygen, and especially the oxygen in solution, causes oxidation of the hydriodic acid formed, and the iodine thus liberated accelerates the action. The error thus caused in the estimation of chlorate may be obviated by conducting the operation in the absence of oxygen. The reaction between hydrochloric acid and potassium chlorate proceeds at the ordinary temperature only in the presence of a considerable excess of hydrochloric acid and is quickly completed; chlorates may be estimated in this way. The substitution of cadmium iodide for potassium iodide has no special advantage, whilst aluminium iodide and mercuric iodide are unsuitable. An acceleration of the reaction was not observed when antimony chloride or cerium sulphate was present. The action is retarded by the addition of water. A. McK.

Estimation of Iodine in Soluble Iodides, also in the presence of Bromides and Chlorides. HUGO DITZ and BENJAMIN M. MARGOSCHES (*Chem. Zeit.*, 1902, 28, 1191—1194).—The solution containing the iodide is mixed with a sufficiency of potassium iodate and then with a slight excess of dilute sulphuric acid. The liberated iodine is extracted with toluene and finally titrated with sodium thio-sulphate. If a known amount of iodate has been added, the excess of this may be estimated in the aqueous liquid by adding potassium iodide and dilute sulphuric acid and titrating with sodium thiosulphate. The shaking with toluene may even be omitted and the iodine expelled by distillation, when the distillate, which is collected in a solution of potassium iodide, may be at once titrated; as, however, this renders the process somewhat tedious, it is more convenient to boil off the iodine and titrate the residual iodate.

If bromides or chlorides are present, the same process applies if the iodine is estimated in its toluene solution and not indirectly in the aqueous liquid. If the excess of iodate is to be estimated in the aqueous liquid after shaking with toluene, acetic acid should be substituted for sulphuric acid. L. DE K.

Estimation of Sulphur by Aid of Sodium Peroxide. ALBERT NEUMANN and JOSEPH MEINERTZ (*Zeit. physiol. Chem.*, 1904, 43, 37—40. Compare Düring, *Abstr.*, 1897, ii, 63).—The substance is fused in a nickel crucible with a mixture of sodium and potassium carbonates and sodium peroxide. The peroxide should be added gradually in 3 or 4 distinct portions. It is found that a gas flame may be employed without causing error. J. J. S.

Estimation of Sulphates in Vegetable Products. GEORGE S. FRAPS (*Chem. Centr.*, 1904, ii, 1433; from *Rep. Chemist North Carolina Agric. Experim. Stat.*, 1902, 1903).—Five grams of the substance are treated for half an hour with 50 c.c. of 1 per cent. hydrochloric acid, and the residue is washed with the same acid until the filtrate measures

about 250 c.c. This is then heated to boiling and precipitated with barium chloride as usual. A number of results are communicated.

L. DE K.

Apparatus for the Estimation of Nitrogen. ÉMILE NICOLAS and DELAUD (*Bull. Soc. chim.*, 1904, [iii], 31, 1193—1194).—This apparatus is a slightly modified form of that described by Porcher and Brisac (*Abstr.*, 1903, ii, 179).

T. A. H.

Sodium Peroxide in Organic Analysis. FRITZ VON KONEK and ARTHUR ZÖHLS (*Zeit. angew. Chem.*, 1904, 17, 1887. Compare *Abstr.*, 1904, ii, 775).—As much as 90 per cent. of the nitrogen in organic substances, which are difficult to burn and which are rich in nitrogen, may be converted into nitrate by means of sodium peroxide.

A. McK.

Rapid Estimation of Nitrogen in Steel or Iron. HJALMAR BRAUNE (*Chem. Centr.*, 1904, ii, 1167; from *Oesterr. Zeit. Berg. Hütt.*, 52, 491).—One gram of the sample is dissolved in 10 c.c. of ammonia-free hydrochloric acid of sp. gr. 1.124, and the filtered solution introduced into a distilling flask containing 250 c.c. of boiling water and 20 c.c. of an alkali hydroxide solution sufficiently strong to neutralise the acid. The distillate is then "Nesslerised" in the usual manner.

L. DE K.

Estimation of Ammonia and Amides. JEAN EFFRONT (*Ber.*, 1904, 37, 4290—4295).—The reaction between alkali hypochlorites and nitrogen compounds may be more accurately followed by determining the loss of active chlorine than by measuring the nitrogen evolved. Amines, imines, nitriles, amides, and amino-acids react with sodium hypochlorite, the active chlorine disappearing being proportional to the weight of organic compound added; tetra-alkylammonium compounds and betaine do not react. A detailed method of carrying out the determination is described.

Ammonia is completely oxidised by sodium hypochlorite at the ordinary temperature (compare Thiele, *Abstr.*, 1893, ii, 317), the nitrogen evolved containing a trace of nitrogen chloride. The ammonia in samples of water may be determined by this method to 0.2 milligram per litre. Proteids may also be determined in water after expelling free ammonia by boiling with sodium carbonate. Proteids show a constant reducing power towards hypochlorites, peptones also show a constant, but lower, reducing power.

C. H. D.

Estimation of Ammonia in Vegetable Products, Beets, &c. EUGENE SELLIER (*Chem. Centr.*, 1904, ii, 1433—1434; from *Bull. Assoc. Chim. Sucr. Dist.*, 21, 1223—1232).—Ammonia may be completely expelled from beetroot juice by the author's magnesia process (*Abstr.*, 1903, ii, 329). In the presence of oxamide, the distillation with magnesia should take place below 40°. Liquids containing urea should be distilled below 80°. Acid ammonium urate

should be treated for a short time with dilute hydrochloric acid and then distilled with magnesia at 36—42°. As hydrochloric acid, however, may hydrolyse urea, the author recommends distilling urine or sediments containing acid urates with calcium oxide at a moderate temperature. Methylamine, if present, partially passes over with the ammonia. If the products should happen to contain magnesium ammonium phosphate, they should be digested for some time with dilute acids; the ammonia will then be completely expelled by boiling with magnesia, but not at a lower temperature. L. DE K.

Electrolytic Estimation of Nitric Acid with a Rotating Anode. LESLIE HOWARD INGHAM (*J. Amer. Chem. Soc.*, 1904, 26, 1251—1255).—The author has tried a process suggested in 1890 by Vortmann (Abstr., 1890, 1467) for the electrolytic estimation of nitric acid and obtained satisfactory results. The solution of the nitrate is mixed with a known volume of standard sulphuric acid, a definite amount of copper sulphate is added, and the mixture submitted to electrolysis. The ammonia formed by the reduction of the nitrate neutralises a portion of the acid, and from the amount of free acid left (which includes that of the copper sulphate) the amount of nitric acid is readily calculated.

The best conditions for a successful experiment were found to be 25 c.c. of copper sulphate solution (= 0.2533 gram of copper), 0.5 gram of potassium nitrate, 25 c.c. of normal sulphuric acid; 9 volts, 4 amperes, time 30 minutes, speed of rotating anode, I [$\frac{1}{2}$ = about 230 revolutions per minute]. L. DE K.

The Evolution of Hydrogen for Marsh's Arsenic Test. CARL MAI and H. HURT (*Zeit. anal. Chem.*, 1904, 43, 557—559).—To accelerate the evolution of hydrogen from zinc and sulphuric acid, it is usual to add a small quantity of a salt of some electro-negative metal. Many of these, however, diminish the sensitiveness of the test, copper and platinum seeming to be the only unexceptionable agents. With the former, the evolution of gas is more regular than with the latter. Iron in any form must be most carefully avoided, since in its presence considerable quantities of arsenic may be overlooked. M. J. S.

Detection of Arsenic in the Ashes of Cremated Bodies. CARL MAI (*Zeit. anal. Chem.*, 1904, 43, 617—619).—On the occasion of the examination of the ashes of a cremated body, the larger bone fragments, after careful cleaning, were found to be absolutely free from arsenic, whilst the mixed pulverulent portion of the ash, in which iron was also present, was highly arsenical. Some iron nails and screws found in the urn also contained much arsenic, and it is assumed that the presence of that element in the miscellaneous powder was entirely due to the metals employed in the construction of the coffin. From a forensic point of view, it is advisable that neither metal nor pigments should be used in coffins intended for cremations.

M. J. S.

Improvement of Drown and Shimer's Method of Estimating Silicon in Irons. J. THILL (*Zeit. anal. Chem.*, 1904, 43, 552—553).—If it is attempted to accelerate the tedious evaporation of the iron solution by substituting the direct heat of a lamp for that of the water-bath, there is danger of loss from bumping and spirting. The addition of ammonium chloride obviates this difficulty. The author's practice is as follows: a litre of concentrated sulphuric acid is mixed with an equal volume of water, and (after cooling) a litre of nitric acid of sp. gr. 1.4 and a solution of 240 grams of ammonium chloride in a litre of water are added. Of this reagent, 50—70 c.c. are used for dissolving 1—2 grams of iron. Solution and evaporation can then be carried on in a beaker over a Bunsen burner with interposed wire gauze, and an estimation completed within an hour. M. J. S.

Qualitative Detection of Silica. JULIUS PETERSEN (*Zeit. anal. Chem.*, 1904, 43, 619—623).—A modification of the method suggested by Daniel (Abstr., 1904, ii, 289) permits the detection of 2.5 mg. of silica with certainty. In a small platinum crucible is placed a mixture of the substance (0.5 gram) with cryolite (0.25 gram), a few milligrams of magnesite, and some concentrated sulphuric acid. The crucible is lowered to the bottom of a test-tube, to which is then fitted a cork carrying a glass rod nearly reaching the crucible. The rod is flattened at its lower end, which is covered with asphalt varnish, and from it a drop of water hangs. The whole of the glass rod and the interior of the test-tube have first been coated with collodion containing 2 vols. per cent. of castor oil. This film protects the glass completely from the action of hydrofluoric acid. The bottom of the tube is then plunged into water of 60°. At this temperature, the formation of silicon fluoride is sufficiently rapid to give a white film on the surface of the drop of water in five minutes. M. J. S.

Estimation and Separation of Calcium in presence of Phosphoric Acid. K. K. JÄRVINEN (*Zeit. anal. Chem.*, 1904, 43, 559—562).—The estimation of calcium in presence of phosphoric acid is liable to two sources of error: incomplete precipitation of the lime and contamination of the precipitate with phosphoric acid. The following mode of operating gives fairly satisfactory results: the solution, which must be as free as possible from ammonium salts, is mixed with ammonia until calcium phosphate just begins to precipitate, and the precipitate is redissolved by a drop of hydrochloric acid. The liquid is heated to boiling and poured slowly into a mixture of equivalent quantities of ammonium oxalate and oxalic acid. Ammonia, not stronger than 1 per cent., is then added drop by drop until the mixture is alkaline and the estimation is finished in the usual manner.

M. J. S.

Estimation of Calcium Oxide in Burnt Lime. Solubility of Calcium Carbonate in Solutions of Ammonium Nitrate. GEORG BERJU and WLADISLAUS KOSINENKO (*Landw. Versuchs-Stat.*, 1904, 60, 419—425).—Bodenbender and Ihlee's method for determining calcium oxide in burnt lime (*Zeit. Rübenzuckerind.*, 1879) by boiling

with ammonium nitrate can give correct results only under certain conditions, owing to the varying amounts of calcium carbonate dissolved.

It is found that calcium carbonate is practically insoluble in $N/5$ ammonium nitrate when the mixture of carbonate and oxide contains 8 per cent. or more of the latter. According to the amount of carbonate present (determined with a Scheibler apparatus), 3—5 grams of substance are treated with 1 litre of $N/5$ ammonium nitrate in a rotatory apparatus turning about 40 times a minute. The calcium oxide is afterwards determined in the usual manner in an aliquot portion of the filtered or subsided solution.

N. H. J. M.

Use of a Rotating Anode in the Electrolytic Estimation of Zinc. LESLIE H. INGHAM (*J. Amer. Chem. Soc.*, 1904, 26, 1269—1283).—A lengthy investigation as to the best and quickest method of electrolytic zinc assay. The ore is oxidised with nitric acid and repeatedly evaporated with hydrochloric acid, and the iron is removed by a double precipitation with ammonia. The ammoniacal filtrate, after adding some more ammonium chloride, is then submitted to electrolysis, using a rotating anode; for working details, the original paper should be consulted. Good results are also obtained by the electrolysis of solutions containing sodium acetate or formate. L. DE K.

Volumetric Estimation of Lead. GUIDO CERVI (*Chem. Centr.*, 1904, ii, 1343—1344; from *L'Industria Chimica*, 6, 289—290).—A slight modification of the process recommended by Guess (*Trans. Amer. Inst. Min. Eng.*, 1904).

The neutralised solution of the lead is acidified with acetic acid, sodium acetate is added, the solution is heated to boiling, and the lead precipitated with standard solution of potassium dichromate. When cold, the liquid is diluted to a definite volume and in an aliquot part of the filtrate, the excess of dichromate is estimated as usual by adding dilute sulphuric acid and potassium iodide and titrating the liberated iodine with standard sodium thiosulphate. In the presence of antimony or iron, the lead should be first separated as sulphate, which is then dissolved and titrated.

L. DE K.

[Analysis of] Commercial Lead. AUGUSTE HOLLARD and L. BERTIAUX (*Bull. Soc. chim.*, 1904, [iii], 31, 1124—1128. Compare Abstr., 1899, ii, 523).—Five grams of commercial lead are dissolved in 86 c.c. of nitric acid of 36° B. previously diluted with water. The liquid is made up to 300 c.c. and the lead removed as the peroxide, using a current of 0.2 ampere (compare Abstr., 1903, ii, 294). Five c.c. of sulphuric acid are then added to the lead-free liquid, and this is evaporated down until sulphuric acid fumes are copiously evolved; it is then diluted to 300 c.c. and the copper determined electrolytically, the precautions already indicated (Abstr., 1904, ii, 682) being taken to obtain a copper deposit free from arsenic, antimony, or bismuth. Nickel and zinc are separately estimated in the residual liquid by the process previously described (Abstr., 1903, ii, 335; 1904, ii, 92 and 682), and iron by titration with iodine (Abstr., 1904, ii, 368 and 592).

For the estimation of arsenic and antimony, a fresh portion of lead is treated with sulphuric acid, and the arsenic separated by distillation after the addition of ferrous sulphate and hydrochloric acid (Abstr., 1900, ii, 438). The residual liquid is placed in a flask having the bottom coated outside with fireclay, and to it is added zinc chloride solution of sp. gr. 2; the antimony chloride is distilled off in a current of hydrogen chloride and finally estimated electrolytically. From a hot nitric acid solution of the lead, silver is precipitated as the chloride, the latter is dissolved in potassium cyanide solution, and the metal determined electrolytically. Sulphur is precipitated as barium sulphate from a nitro-hydrochloric acid solution of the original material. Bismuth is separated as the basic nitrate, which is then converted into sulphide and freed from arsenic, antimony, and tin by means of ammonium hydrosulphide, and is finally estimated by electrolysis of a solution of the sulphate (Abstr., 1904, ii, 684). The tin obtained as the sulphide in the separation of the bismuth is freed from antimony by electrolysis in presence of potassium cyanide, and finally determined electrolytically in hydrochloric acid solution in presence of ammonium oxalate. A tabular statement showing the composition of thirteen samples of commercial lead is given in the original.

T. A. H.

Electrolytic Separations possible with a Rotating Anode.

DONALD S. ASHBROOK (*J. Amer. Chem. Soc.*, 1904, 26, 1283—1290).—A paper unsuitable for adequate abstraction. Working details are given as to the electrolytic separation of *copper* from aluminium, antimony, arsenic, cadmium, chromium, cobalt, iron, lead, magnesium, manganese, nickel, uranium and zinc; *cadmium* from aluminium, chromium, cobalt, iron, magnesium, manganese, nickel and zinc; *silver* from aluminium.

L. DE K.

Electrolytic Estimation of Copper. AUGUST KUFFERATH (*Zeit. angew. Chem.*, 1904, 17, 1785—1786).—About 1.5 grams of the substance containing copper are dissolved in dilute sulphuric acid with the aid of nitric acid; if an excess of the latter is carefully avoided, there is no need for evaporating to dryness. After diluting to about 130 c.c., 2 grams of formaldehyde are added, and the copper is deposited as usual by heating at 60—65° and using a current of 2.5—3 amperes and 2 volts. Without interrupting the current, the deposit is washed first with water, then with alcohol, and finally with ether, and is then dried in a vacuum over sulphuric acid and weighed. Iron, nickel, and cobalt are not deposited in the presence of formaldehyde.

L. DE K.

Titration of Copper by Potassium Iodide, and Applicability of the Method in presence of Iron and Arsenic. L. MOSER (*Zeit. anal. Chem.*, 1904, 43, 597—616).—Both the original method of De Haen and Rümpler and Low's modifications (Abstr., 1896, ii, 450) are affected by sources of error, and the variation suggested by Litterscheid (Abstr., 1902, ii, 531) is useless in presence of iron or

arsenic. The author has reinvestigated De Haen's method, employing thiosulphate for the titration of the iodine. When free acids are absent, the results are only satisfactory if the solutions are sufficiently concentrated, but in presence of free sulphuric acid correct results are obtained, even when the dilution and amount of free acid are largely varied. Hydrochloric and nitric acids as acidifying agents are inadmissible, but acetic acid may be used. Although the action of potassium iodide on a cupric salt indubitably consists at first in the formation of cupric iodide, in the presence of free acid the decomposition into cuprous iodide and free iodine is so rapid and complete that titration may be commenced two minutes after making the mixture; a delay of ten minutes does not materially affect the results, but after an hour higher numbers are obtained. The following is the form in which the process is recommended: the copper solution (50 c.c. containing about 0.15 gram of copper as sulphate) is placed in a 300 c.c. stoppered bottle; 5 c.c. of 10*N* sulphuric acid and 2 grams of solid potassium iodide are added and the bottle is shaken for two minutes. The free iodine is then titrated with *N*/10 thiosulphate, adding starch when near the end.

To render the method applicable in presence of iron and arsenic, the solution of the metals (as sulphates) is treated with an excess of sodium pyrophosphate sufficient to redissolve the precipitate at first formed. If the original solution contained free sulphuric acid, some sodium acetate is added, then 4—5 grams of potassium iodide and 5—10 c.c. of 80 per cent. acetic acid. In these circumstances, the copper alone liberates iodine, but to obtain good results it is advisable to avoid dilution as far as possible, wherefore solid sodium pyrophosphate should be used for the precipitation, and if the amount of iron exceeds that of copper by more than one-third, the quantity of potassium iodide should be increased; a somewhat longer time (15 minutes) is allowed before titrating, and the thiosulphate run in very slowly.

M. J. S.

Detection and Estimation of Minute Quantities of Mercury. CONSTANTIN ZENGELIS (*Zeit. anal. Chem.*, 1904, 43, 544—547).—For the detection of mercury in urine, the urine is feebly acidified with hydrochloric acid and left in contact for 12 hours with a spiral of copper and platinum wires. The spiral is then washed with dilute sodium hydroxide, water, alcohol, and ether, and dried completely over sulphuric acid. It is then thrust to the bottom of a narrow test-tube, the upper part of which is moistened with a solution of iodine in anhydrous ether. Holding the tube horizontally, the coil is heated, and the evolved mercury vapour is arrested by the ring of iodine solution and converted into mercuric iodide. Complete absence of water is indispensable: 0.2 milligram of mercury can be detected in 200—300 c.c. of urine. For quantitative estimation, the urine is boiled with an excess of sodium hydroxide and a little of a reducing sugar. The phosphate precipitate is dissolved in nitric acid and the solution electrolysed at 40—50° with a weighed piece of platinum foil as cathode.

M. J. S.

Detection and Estimation of Traces of Mercury in Urine with the aid of the Nernst Balance. ERNST JÄNECKE (*Zeit. anal. Chem.*, 1904, 43, 547—552).—It is often desirable to be able to estimate with accuracy quantities of mercury not exceeding 0.5 mg. per litre of urine. The use of the Nernst balance (*Abstr.*, 1903, ii, 371) enables this to be done with 250 c.c. of the urine. The organic matter is destroyed by heating the urine with potassium chlorate and hydrochloric acid, and the mercury is then precipitated on a spiral of clean copper wire. The spiral is dried and strongly heated in a test-tube which has been drawn out to a capillary at the open end. The mercury is thus collected in the capillary tube. This is then crushed under a mixture of nitric and sulphuric acids, and, after heating to dissolve the mercury, a little potassium sulphate is added, and the solution, measuring 10 c.c., is electrolysed with a coil of gold wire as cathode and a spiral of platinum wire as anode. These coils are conveniently kept from contact during the electrolysis by placing one inside and the other outside a short glass tube open at both ends. The gold wire is weighed before and after the electrolysis by substituting it for the scale-pan of the Nernst balance. Since the gold absorbs hydrogen during the electrolysis, a correction is made by inserting into the circuit a second similar coil in a cell free from mercury. The actual presence of mercury on the gold should be confirmed by expelling it into a capillary tube containing a trace of iodine. The author has succeeded, by this method, in detecting 0.01 mg. of mercury which had been added to two litres of urine. M. J. S.

A Modified Form of the Persulphate Method of Estimating Manganese in Iron and Steel. H. PROCTER SMITH (*Chem. News*, 1904, 90, 237).—The following modification of this process is described: 0.2 gram of the sample, and the same weight of a steel containing a known quantity of manganese are both placed in test-tubes and each gently heated with 10 c.c. of nitric acid of sp. gr. 1.2 until dissolved. The solutions are boiled to expel red fumes, and 10 c.c. of silver nitrate solution (1.7 grams per litre) and about 1 gram of ammonium persulphate are added. After heating until the latter is nearly dissolved, the sides of the tubes are washed down with water and the contents cooled. The perfectly cold pink solutions are then transferred to china basins and titrated with sodium arsenite solution. The latter is prepared by dissolving 5 grams of arsenious oxide and 15 grams of sodium hydrogen carbonate in 250 c.c. of boiling water and diluting to 1 litre. Forty c.c. of this solution diluted to 500 c.c. form the titration solution, which, for each set of analyses, must be standardised on a steel containing a known quantity of manganese. W. P. S.

Volumetric Estimation of Iron. NAZARENO TARUGI and S. SILVATICI (*Chem. Centr.*, 1904, ii, 1341—1342; from *Boll. Chim. Farm.*, 43, 637—641).—The solution, which must contain the iron in the ferric state, is carefully neutralised with sodium hydroxide, and after adding some potassium thiocyanate the liquid is titrated with *N*/10 potassium oxalate until the colour changes to yellowish-green. One c.c. of the

oxalate solution = 0.00186673 gram of metallic iron. It is advisable to make a blank experiment using 5 c.c. *N*/10 ferric chloride.

L. DE K.

Colorimetric Estimation of Iron in Blood. ADOLF JOLLES (*Zeit. anal. Chem.*, 1904, 43, 537—539).—The author's most recent modification of his original method (Abstr., 1897, ii, 126) consists in comparing the colour of the iron solution obtained from 0.05 c.c. of blood with that of the glass wedge of Fleischl's hæmometer, and he regards the apparatus for this form of estimation, to which he gives the name "clinical ferrometer," as the simplest and most convenient for clinical purposes (compare Oerum, Abstr., 1904, ii, 449). Whereas, in general, the percentage of iron in the blood is proportional to that of the hæmoglobin, in many pathological conditions, such as anæmia, icterus, &c., the relation undergoes a marked alteration. M. J. S.

Analysis of Commercial Tin and its Alloys. AUGUSTE HOLLARD and L. BERTIAUX (*Bull. Soc. chim.*, 1904, [iii], 31, 1128—1131).—A complete scheme for the analysis of commercial tin is given. Arsenic is determined by distillation with hydrochloric acid and ferrous sulphate, the distillate being titrated with iodine (Abstr., 1900, ii, 438). The copper, bismuth, and lead are separated from the tin by precipitation as sulphides in presence of ammonium sulphide, and the bismuth and lead from copper by precipitation as sulphides in presence of ammonia and potassium cyanide. Finally, the lead and bismuth are separated and estimated electrolytically as already described (Abstr., 1904, ii, 684). Antimony is estimated by dissolving 1 gram of the tin in nitro-hydrochloric acid, evaporating down repeatedly with hydrochloric acid, adding a little sodium hydroxide to the residue, and electrolysis under the conditions previously described (Abstr., 1903, ii, 455). For the estimation of copper and sulphur, 5 grams of tin are treated with nitric acid and the whole evaporated to dryness; the residue is washed thoroughly with water containing a little nitric acid, and in these washings the copper is estimated electrolytically and the sulphur by precipitation as barium sulphate. For lead-tin alloys, 1 gram of the alloy is treated with 50 c.c. of nitric acid (water should be added if the alloy is rich in lead) in presence of 10 grams of copper. The liquid is diluted to 300 c.c. and warmed to cause the tin oxide to agglomerate. When cold, the lead is estimated electrolytically as the peroxide (Abstr., 1899, ii, 523; 1904, ii, 294); to obtain the last traces of lead, the anode should be withdrawn when the greater part of the lead has been deposited, and the mixture shaken and left in a warm place for a time. The anode should then be replaced and the electrolysis continued. T. A. H.

Estimation and Separation of Gold in the Electrolytic Way. SARAH P. MILLER (*J. Amer. Chem. Soc.*, 1904, 26, 1255—1269).—A lengthy article, unsuitable for adequate abstraction, showing the conditions under which gold can be satisfactorily separated from iron, cadmium, silver, zinc, cobalt, nickel, and copper. The gold is deposited

from solutions containing either potassium cyanide, phosphoric acid, or sodium sulphide.
L. DE K.

Inadmissibility of Soap for Estimating Hardness of Ferruginous Water. A. GAWALOWSKI (*Zeit. anal. Chem.*, 1904, 43, 533—536).—A sample of well-water containing 0.036 gram of ferrous oxide per litre in the form of sulphate gave, on titration with soap solution, results widely at variance with the amounts of calcium and magnesium estimated gravimetrically, neither could concordance be established by including in the calculation the amount of soap consumed by the iron present. An attempt to titrate with soap, after the removal of the iron by potassium ferrocyanide, also failed to give a satisfactory result.
M. J. S.

Estimation of Ammonia and Proteid-Nitrogen in Waters. JEAN EFFRONT (*Chem. Centr.*, 1904, ii, 1253—1254; from *Mon. Sci.*, [iv], 18, 669—674).—An accurately titrated solution of bleaching powder is mixed with a definite volume of the sample of water to be tested, and the loss in active chlorine represents the nitrogen of the ammonia and proteids. The experiment is then repeated with water from which the ammonia has been expelled by evaporation with sodium hydroxide; the result is the proteid-nitrogen only.

The active chlorine is estimated by adding excess of sodium arsenite and titrating the excess with standard iodine.
L. DE K.

Addenda to Simple Method for Decarbonising Substances. Estimations in the Decarbonised Product. ALBERT NEUMANN (*Zeit. physiol. Chem.*, 1904, 43, 32—36. Compare Abstr., 1903, ii, 243).—Further manipulative details are given for the processes and estimations already described.
J. J. S.

Alkaloid Reactions. IV. Morphine. C. REICHARD (*Chem. Zeit.*, 1904, 28, 1102—1105. Compare Abstr., 1904, ii, 791, 992).—The author communicates a new reaction for morphine which is quite characteristic. If morphine is gently warmed with strong sulphuric acid containing some arsenious or arsenic acid, an intense and permanent purple coloration is developed. In practice, it is best to make a solution of arsenious acid in strong aqueous sodium hydroxide; to this may be added first the morphine and then an excess of very strong sulphuric acid.

Morphine is also coloured red by antimonious chloride without using sulphuric acid. Stannous chloride in conjunction with sulphuric acid also causes the reaction.
L. DE K.

Mechanical Analysis of Soils and Sub-soils by Centrifugal Action; with Notes on Treatment of Samples. J. R. KILROE (*Econ. Proc. Roy. Dublin Soc.*, 1904, 1, 223—230).—A centrifugal apparatus is described by means of which mechanical separations can be made rapidly and with considerable accuracy. The amount of soil employed for a determination is 20—30 grams, and very little distilled water is required.
N. H. J. M.

General and Physical Chemistry.

Enhanced Lines of Titanium, Iron, and Chromium in the Fraunhoferic Spectrum. Sir J. NORMAN LOCKYER and F. E. BAXANDALL (*Proc. Roy. Soc.*, 1904, **74**, 255—267).—The contents of this paper are summarised as follows. The enhanced lines of titanium and iron are practically all represented in the Fraunhofer spectrum, but in some cases the corresponding solar lines are compound and only partly due to one or other of these metals. The corresponding solar lines are, generally speaking, comparatively weak ones. The majority of the chromium enhanced lines occur in the solar spectrum, although some appear to be missing. Some of the Fraunhofer lines correspond with metallic lines special to the spark spectrum, and lacking in the arc, and probably for this reason they were left unoriginised by Rowland. J. C. P.

Spectrum Regularities and the Atomic Weight of Radium. GEORGE RUDORF (*Zeit. physikal. Chem.*, 1904, **50**, 100—110. Compare Runge and Precht, *Abstr.*, 1903, ii, 346; Watts, *Abstr.*, 1904, ii, 720).—The author finds that frequency differences (d) and atomic weights (A) are not exactly related according to the equation $d/A^n = \text{const.}$; hence the formula $\log A = a + b \log d$ is not exactly valid, and any considerable extrapolation based on the straight line formula may lead to error. It is shown that certain graphical relationships exist between the values of A and $100d/A^2$, which permit of the calculation of d for other elements. The value 225 should for the present be taken as the atomic weight of radium. J. C. P.

Racemism. GIUSEPPE BRUNI (*Atti R. Accad. Lincei*, 1904, [v], **13**, ii, 373—381. Compare Bruni and Finzi, this vol., ii, 2; Bruni and Padoa, *Abstr.*, 1902, i, 343).—The freezing-point surface and the course of the isotherms of solutions of mixed optical isomerides give a clue to the molecular condition of the dissolved substances and indicate the existence or non-existence of racemic molecules in the liquid. On adding to a *p*-xylene or ethylene bromide solution of methyl diacetyl-tartrate increasing quantities of methyl diacetyl-racemate, it is found that the freezing-point depressions are always less than the normal values; the molecular weights are hence abnormally great, so that there must be a certain number of undissociated racemic molecules in solution. The abnormality diminishes as the concentration of the racemic compound increases, which must be attributed to the fact that the excess of the diacetyl-tartrate undergoes a continuous relative decrease, its influence in retarding the dissociation thus becoming less. If temperatures are taken as ordinates and total concentrations as abscissæ, the freezing points of the solutions of methyl diacetyl-tartrate and diacetyl-racemate and the cryohydrate point of the mixed solutions lie on a straight line, if the racemic compound undergoes complete

dissociation in the solution; where there is partial racemisation, this is no longer the case. The three dimensional curves, obtained with the concentrations of the *d*- and *l*-compounds and the temperature as co-ordinates, also have different forms for the cases where there is partial racemisation and complete dissociation.

Methyl diacetylracemate also exists partially non-dissociated in solution in diphenylmethane or naphthalene, in the latter solvent at temperatures as high as 80°. The freezing-point constant for diphenylmethane is 71, and not 67 as was stated by Eijkman (*Abstr.*, 1890, 324). Ethyl *r*-dibromophenylpropionate is partially non-dissociated in naphthalene solution in presence of the *d*-compound. T. H. P.

Possibility of Resolving Racemic Compounds by Circularly Polarised Light. The Primary Production of Optically Active Substances. ALFRED BYK (*Zeit. physikal. Chem.*, 1904, 49, 641—687; *Ber.*, 1904, 37, 4696—4700).—As a starting point, Cotton's experiment is taken, according to which the *d*- and *l*-components of Fehling's solution possess different coefficients of optical absorption for circularly polarised light of definite sign. It can also be shown that the positions of the maxima of optical absorption and of photochemical sensitiveness coincide, and the conclusion is drawn that the extent of decomposition of these sensitive compounds in circularly polarised light is not the same for each. On the strength of Ostwald's work on the independent optical absorption of the ions in dilute solution, the author draws the further conclusion that this difference of sensitiveness persists in the inactive Fehling's solution, and must therefore result in this solution gradually becoming active under the decomposing influence of circularly polarised light. For the details of each step in this indirect proof, reference must be made to the original.

The extensive occurrence of optically active compounds in nature may thus be referred to the production in excess of one kind of circularly polarised light at the earth's surface. This result is reached by the reflection of the plane polarised rays of sunlight from the surface of the sea, assisted by the influence of the earth's magnetism.

Incidentally it was found that the same effect was produced by *d*- and by *l*-circularly polarised light on sensitive, optically active photographic preparations (silver tartrate paper and silver bromide plates sensitised with chlorophyll). The progressive dissociation with dilution of a racemic salt was followed in the case of Fehling's solution, and it was shown that the production of the racemic salt obtained by mixing *d*- and *l*-Fehling's solutions is accompanied by a change of colour. J. C. P.

Formation of Salts in Solution, especially in the Case of Substances Exhibiting Tautomerism (Pseudo-acids, Pseudo-bases). I. JULIUS W. BRÜHL and HEINRICH SCHRÖDER (*Zeit. physikal. Chem.*, 1904, 50, 1—42).—Full details are given of the spectrochemical investigation of the esters of camphorcarboxylic acid and the sodium derivatives formed from these. The chief conclusions arrived at have already been reported (*Abstr.*, 1904, i, 646 and 969). As a further and secondary result of the investigation, following from observations

made on the variation of the specific refraction of sodium in methyl and ethyl alcohols and its constancy in amyl alcohol (see Abstr., 1904, i, 969), it seems that the value of the specific refraction for the sodium ion is 12—15 per cent. less than the value for sodium in an unionised compound. J. C. P.

Luminescope for Comparing Substances under the Influence of Radium Rays. C. S. STANFORD WEBSTER (*J. Soc. Chem. Ind.*, 1904, 23, 1185—1186).—The instrument has been designed to facilitate the comparison of different substances in regard to their “glow” and scintillating power under the influence of radium rays. It resembles the spinthariscopes, but the draw tube with the system of lenses is mounted on one side of a circular metal box which contains a metal disc carrying four screens. By turning a handle, the disc can be rotated and the screens brought into position under the observation tube as required. One of the screens is temporarily fixed by wire-spring clips and can be replaced at will. H. M. D.

Induced Radioactivity. KARL A. HOFMANN, L. GONDER, and VALENTIN WÖFLI (*Ann. Physik*, 1904, [iv], 15, 615—632. Compare Abstr., 1902, ii, 261, 397; 1903, ii, 402).—Although a uranium salt can be separated into a more and a less active portion, the two portions finally exhibit the same activity (compare Becquerel, Abstr., 1902, ii, 117), so that uranium is itself a radioactive element. When small quantities of salts of other metals are dissolved in concentrated solutions of uranium nitrate, and, after a few weeks, are separated from the uranium by chemical methods, the precipitated sulphate, sulphide, or oxalate, as the case may be, is found to have an induced radioactivity, which gradually disappears. The degree of activity of the precipitate depends on the nature of the inactive metal it contains; thus the activity transmitted to lead and bismuth sulphides is much greater than that transmitted under similar conditions to the sulphides of palladium, platinum, and mercury. When two inactive metals acquire an induced activity from the same uranium solution, their relative activity is independent of the order in which they have been separated from the solution. When the metals are arranged according to the relative activity induced under the above conditions, the order is roughly the same, whether uranium or radium is used as the inducing agent, but is quite different when radiolead or radiobismuth is the inducing agent. For iridium, palladium, rhodium, and platinum are distinguished by the marked activity which is induced in them by radiolead. The chloride in each case was kept for three weeks in common solution with radiolead chloride, and then the metal was precipitated by formaldehyde or hydroxylamine. The α -activity thus induced on these metals is removed on ignition at a bright red heat, but the β -activity is only slightly diminished by that treatment. This observation leads to the suggestion that the α -activity is occluded, but, in conflict with this view, it has been shown for platinum that the activity of the metal is not greater than that of the sulphide obtained by precipitation from the same radiolead solution. At the ordinary temperature, the induced β -activity disappears more rapidly than the

α -activity. When the metals palladium, iridium, and silver (platinum and gold in a less degree) in the solid form have been immersed for several days in an active lead chloride solution, obtained from pitchblende and kept at 60°, they exhibit marked radioactivity. When active bismuth salts prepared from pitchblende are used as inducing agents in the manner previously described, they lose their own activity and do not regain it, in contrast to the radiolead preparations. The process of induction is supposed to consist in the emission of particles from the primarily active substance, those particles adhering then to the atoms and ions which are susceptible to the induction. J. C. P.

Action of Radium Rays on Caoutchouc. RUDOLF DITMAR (*Chem. Centr.*, 1904, ii, 1652—1653; from *Gummi-Zeit.*, 19, 3—4. Compare Abstr., 1904, i, 757).—The power of radium rays of penetrating caoutchouc has been examined by Madame Curie's radiographic method. A "concentrated" preparation of de Haen's radium barium bromide was used, but the action of this substance was not sufficiently powerful to induce radioactivity in the caoutchouc itself. The following conclusions have been derived from the results of the experiments of the author and the investigations of Madame Curie. The radium rays (γ -rays) penetrate both crude and vulcanised rubber, but the former more readily than the latter, probably owing to its porosity. Caoutchouc itself may be rendered radioactive (Madame Curie). The loss of activity of caoutchouc in air does not take place in accordance with the law which usually obtains for solids. E. W. W.

Variation of the Resistance of Bismuth in a Feeble Magnetic Field. C. CARPINI (*Nuovo Cim.*, 1904, [v], 8, 171—186).—The variation of the resistance of bismuth in both feeble and strong magnetic fields is a hyperbolic function of the strength of field, and is also a sine function of the angle made by the coil of bismuth with the lines of force. No hysteresis phenomena were observed on changing the strength of field. When an alternating current is employed, the change of resistance is far smaller than with the corresponding direct current. The curves appear to depend in a very complicated manner on the amplitude and period of the alternating current. T. H. P.

Electric Conductivity of Phosphorus Emanation and of Freshly Prepared Gases. EUGÈNE BLOCH (*Ann. Chim. Phys.*, 1905, [viii], 4, 25—144. Compare Abstr., 1903, ii, 206; 1904, ii, 117).—The electric conductivity of dry air which has passed over phosphorus or of freshly prepared gases (such as hydrogen or carbon dioxide obtained by the action of acid on metals or marble respectively) is in each case due to the same cause, namely, the presence of ions which differ in their mobility and their coefficient of recombination from the ordinary ions. M. A. W.

Electrolytic Conductivity of Colloidal Solutions. G. E. MALFITANO (*Compt. rend.*, 1904, 139, 1221—1223).—Carefully purified

colloidal solutions have an electrolytic conductivity greater than that of water; this is, however, due to the small quantity of soluble electrolytes unavoidably present in such solutions, and not to the colloidal granules themselves, which appear to be without electric charge, for the clear liquid obtained after filtering a colloidal solution through a collodion membrane has the same electrolytic conductivity as the original solution or the residual liquid rich in colloidal granules; thus a solution of ferric chloride, which had been heated to 100° and contained 0.371 per cent. of chlorine and 0.132 per cent. of iron, had $k=0.02301$, the clear colourless filtrate contained 0.367 per cent. of chlorine and 0.077 per cent. of iron, and had $k=0.02299$, and the residual colloidal liquid contained 0.380 per cent. of chlorine, 0.182 per cent. of iron, and had $k=0.02273$, and similar results were obtained with colloidal solutions of arsenic pentasulphide, or white of egg.

M. A. W.

Conductivities of Certain Electrolytes in Water, Methyl and Ethyl Alcohols, and Mixtures of these Solvents. Relation between Conductivity and Viscosity. HARRY C. JONES and CHARLES G. CARROLL (*Amer. Chem. J.*, 1904, **32**, 521—583. Compare Jones and Lindsay, *Abstr.*, 1903, ii, 55).—The conductivity of cadmium iodide has been determined at 0° and 25° in water, methyl and ethyl alcohols, and mixtures of water with each of these alcohols. The determinations were made at dilutions varying from 16 to 256. The results show that cadmium iodide does not exhibit a minimum in mixtures of methyl alcohol and water at 25° , but that a minimum appears at 0° in a mixture containing 75 per cent. of the alcohol at concentrations of not less than 64, but disappears at greater dilutions. In mixtures of ethyl alcohol and water at 25° , no minimum is observed.

Determinations of the conductivity of sodium iodide at 0° and 25° in water and in methyl alcohol of 25, 50, and 75 per cent. strength have shown that a minimum is exhibited, but is more pronounced at 0° than at 25° . At 25° , a minimum occurs in 75 per cent. methyl alcohol at a concentration of 32, but beyond this dilution the minima are only observed in the 50 per cent. mixture. At 0° , the minimum appears in the 50 per cent. mixture only.

The conductivity of solutions of calcium nitrate in water, methyl alcohol, ethyl alcohol, and mixtures of each of these alcohols with water was determined at 0° and 25° , but in no case was a minimum observed.

Determinations of the conductivity of hydrogen chloride in methyl alcohol of 50, 69.75, 90, and 100 per cent. strength gave results which show that in each case the molecular conductivity decreases as the concentration increases. In the 69.75 per cent. mixture, a maximum is obtained both at 0° and 25° . In the 90 per cent. mixture, the results are regular, and a limiting value is reached at a dilution of 157.67. It is found that hydrochloric acid shows a minimum both in the 69.75 and the 90 per cent. mixtures. At 25° , the minimum appears at a dilution 178.75, and at 0° it appears at all dilutions.

The conductivity of sodium acetate in acetic acid of 25, 50, 75, and

100 per cent. strengths was determined at 25°, but the results were irregular and led to no definite conclusions.

The dissociation of potassium iodide, sodium iodide, ammonium bromide, ammonium iodide, and lithium nitrate in 50 per cent. methyl alcohol was calculated from conductivity determinations. In the case of potassium and sodium iodides, it was found that the dissociation is greater in the mixture of methyl alcohol and water than in either of the pure solvents, and that the dissociation of potassium bromide is greater in the mixture than in pure water.

The dissociation of hydrochloric acid in methyl alcohol of 69.75 per cent. strength is also greater than in water at the corresponding dilution, but this is not the case for the 90 per cent. alcohol.

The dissociation of potassium and sodium iodides in water, methyl alcohol, and ethyl alcohol is found to agree quantitatively with the hypothesis of Dutoit and Aston (Abstr., 1897, ii, 456).

It is suggested that the greater dissociation found in the 50 per cent. mixture of methyl alcohol and water is due to the presence of a hydrate, $\text{CH}_3\cdot\text{OH}\cdot 3\text{H}_2\text{O}$, formed by the association of four simple molecules, whereas in water the number of molecules associated with one another at the ordinary temperature is less than four.

An explanation has been suggested by Jones and Lindsay (*loc. cit.*) to account for the occurrence of the minimum point in the conductivity values. It is now shown, however, that this explanation is not altogether satisfactory, and that the decrease in the conductivity of electrolytes in binary mixtures of various alcohols and water, sometimes accompanied by a minimum conductivity, is due mainly to a diminution in the fluidity, produced on mixing the solvents, and the consequent decrease in ionic mobility.

The hypothesis of Kohlrausch (Abstr., 1903, ii, 403) that each ion is invested with an atmosphere of the solvent of considerable thickness is shown to be true in the case of binary electrolytes, not only in aqueous solutions, but also in methyl and ethyl alcohols.

The relation between conductivity, association, and viscosity is discussed, and the hypothesis is put forward that the conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents, such as methyl and ethyl alcohols and acetone, are inversely proportional to the coefficient of viscosity of the solvent and directly proportional to its association factor. This relation has been tested in a number of cases and found to be true in each.

The results of the experiments are tabulated and are also plotted as curves.

E. G.

Relation between the Size of the Molecular Complex and the Temperature-coefficient of Expansion in Different States of Aggregation. WILHELM VAUBEL (*J. pr. Chem.*, 1904, [ii], 70, 503—508).—As the molecular vibrations and the consequent temperature-coefficients of expansion of a substance in the gaseous and in the liquid states of aggregation must be in direct proportion to the size of the molecules, it is proposed to calculate the number of gas-molecules associated in the liquid-molecule from the relation to each other of the coefficients.

The results so obtained agree with those from other methods for chlorine, bromine, phosphorus, bismuth, water, ether, acetone, and methyl, ethyl, and propyl alcohols; in most other cases, the results are too high. Contrary to previous determinations of the molecular weights of homologous series of organic compounds in the liquid state, the value obtained by the present method increases with the vapour density. G. Y.

Effect of Mechanical Vibration on Carbon Dioxide near the Critical Temperature. WALTER P. BRADLEY, A. W. BROWNE, and C. F. HALE (*Physical Review*, 1904, 19, 258—272).—When a system containing both liquid and gaseous carbon dioxide between temperatures of 29° and 31.2° is subjected in a Cailletet apparatus to proper mechanical vibration, a peculiar fog effect is produced. This is due, not to impurities in the gas, but to a change of state in the liquid and vapour phases, resulting respectively in the formation of minute bubbles and drops. The change of state is produced by alternate compression and dilatation effected by the vibrations of a steel rod clamped to the pressure jacket of the apparatus. Under given conditions of temperature, pressure, length of mercury column, and relative volume of the phases, vibrations of a certain definite pitch are required in order to produce the fog effect. The present paper deals with the measurement of variables determining the pitch of the effective vibrations. J. C. P.

Regularities in Homologous Series. OTTO BIACH (*Zeit. physikal. Chem.*, 1904, 50, 43—64).—It is well known that in certain homologous series the melting point alternately rises and falls (compare also Lamouroux, *Abstr.*, 1899, i, 479; Henry, *ibid.*, 735), and in the present paper the author attempts to show that this oscillatory variation is characteristic of all physical constants. When the constants themselves vary more or less regularly, their differences may be found to oscillate, or the differences between these first differences may exhibit the required peculiarity. By way of explanation, the author makes the supposition that the valency of hydrogen is not exactly one-fourth that of carbon. J. C. P.

Rate of Chemical Auto-heating (Adiabatic Reaction Kinetics). GEORGE BREDIG and F. EPSTEIN (*Zeit. anorg. Chem.*, 1904, 42, 341—352).—A theoretical paper in which the following question is discussed. Given a chemically reactive system of the initial concentration a and having at constant temperature the rate constant kT_x , which is variable with the temperature T_x , whilst in the reaction in question the amount of heat, q , is evolved for each formula-weight, g ; it being assumed that the reaction proceeds in a vessel impermeable to heat, so that the system is thus heated or cooled by its own heat of reaction. After what period of time, z , will a definite temperature T_x and at the same time a definite chemical transformation, x , be reached?

To illustrate the equations deduced, the action $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ was studied under the catalytic influence of potassium iodide and, so far as possible, under adiabatic conditions. At a definite time, a

mixture of hydrogen peroxide and potassium iodide was introduced into a Dewar-Weinhold flask and the auto-heating of the system estimated after definite intervals of time.

A. McK.

Some Thermochemical Rules relating to the Possibility and Prognostication of Reactions. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 1005—1009).—A theoretical paper not suitable for abstraction.

M. A. W.

Thermochemical Studies. DANIEL LAGERLÖFF (*J. pr. Chem.*, 1904, [ii], 70, 521—559. Compare Abstr., 1904, ii, 382, 605).—The conclusion of the author's mathematical discussion of the theory of the heat of formation of carbon compounds.

G. Y.

Combustion of Sulphur in the Calorimetric Bomb. H. GIRAN (*Compt. rend.*, 1904, 139, 1219—1221).—The author has measured the heat of combustion of sulphur in oxygen in a calorimetric bomb under varying pressures, estimated the sulphur dioxide and sulphur trioxide in the gaseous products, and calculated the heat of formation of sulphur dioxide under different pressures; the results show that the heat of formation of sulphur dioxide and the proportion of sulphur converted into the trioxide increase with the pressure, and the following table comprises the results:

Pressure.	Heat of formation of SO ₂ .	Ratio of weight of sulphur converted into trioxide to total weight of sulphur.
1 atmos.	69·80 Cal. (by extrapolation)	—
2·5 „	70·43 „	0·142
5 „	71·60 „	0·165
10 „	72·19 „	0·184
15 „	74·45 „	0·188
20 „	75·52 „	0·219
25 „	77·88 „	0·228
30 „	78·41 „	0·272
35 „	80·26 „	0·294
40 „	80·88 „	0·307
45 „	81·13 „	0·312

It is probable that the increase with the pressure in the heat of formation of sulphur dioxide is due to the formation of a higher oxide of sulphur, as the residue contained in the bomb shows the characteristic properties of the anhydride of persulphuric acid.

The heat of formation of sulphur dioxide under atmospheric pressure is 69·80 Cal.

M. A. W.

Villari's Critical Point in the Case of Nickel. K. HONDA and S. SHIMIZU (*Ann. Physik*, 1904, [iv], 15, 855—859).—The authors adhere to their former conclusion (*Ann. Physik*, 1904, [iv], 14, 791), that nickel does not exhibit this critical point.

J. C. P.

Fusion of Dissociating Compounds and the Degree of Dissociation of the Fused Substance. ROBERT KREMANN (*Monatsh.*, 1904, 25, 1215—1269).—From theoretical considerations, it

is shown that, if curves are constructed with melting points as ordinates and molecular percentages of one substance, which forms an additive compound with the other, as abscissæ, the more strongly the additive compound dissociates on melting, the flatter is the curve near the maximum at its melting point.

The melting point of the additive compound is affected less by addition of one of the components than of an indifferent substance, as the former takes part in the equilibrium between the additive compound and its components. The molecular depression of the melting point of the additive compound is calculated from the heat of fusion, or is determined directly by addition of indifferent substances, unless these act as solvents, when the molecular depression produced increases with the dielectric constant.

The extent to which the additive compound dissociates on melting can be determined within 1 per cent. by comparison of the theoretical with the experimental curve. The additive compound of aniline with phenol has the molecular depression of the melting point, $\Delta = 0.278^\circ$, and, when fused, dissociates to the extent of 20 per cent. The curve for mixtures of phenol and picric acid has eutectic points at 36° and 80° for mixtures containing 7 and 59 molecular per cent. respectively of picric acid; the additive compound has $\Delta = 0.401^\circ$ and a dissociation degree of 27 per cent. For mixtures of trinitrotoluene and naphthalene, the curve has eutectic points at 72° and 71° , representing 12 and 85 molecular per cent. respectively of trinitrotoluene; the additive compound melts at 96.5° . The curve for the mixtures of naphthalene and picric acid (compare Saposchnikoff and Rdultowsky, *Abstr.*, 1904, i, 399) has eutectic points at 78° and 111° for mixtures containing 4 and 92 molecular per cent. respectively of picric acid; the additive compound melts at 147° . The mixtures of nitroso-dimethylaniline and aniline show eutectic points at -10° and 75° , representing 2.5 and 90 molecular per cent. respectively of nitroso-dimethylaniline; the additive compound contains 33 molecular per cent. of aniline, melts at 93° , has $\Delta = 0.202^\circ$, and, when melted, dissociates to the extent of 15 per cent. G. Y.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. ROBERT KREMANN (*Monatsh.*, 1904, 25, 1271—1310. Compare foregoing abstract).—The melting point curve of mixtures of 2:4-dinitrotoluene and naphthalene has eutectic points at 53° and 56° for mixtures containing 28 and 69 molecular per cent. respectively of naphthalene; the maximum for the additive compound is 59° . The curve for mixtures of nitrotoluene and naphthalene falls to one eutectic point at 27° for a mixture containing 38 molecular per cent. of nitrotoluene. The curve for mixtures of trinitrobenzene and naphthalene falls to eutectic points at 77° and 114° for mixtures containing 8 and 88 per cent. respectively of naphthalene; the maximum for the additive compound (Hepp, *Abstr.*, 1883, 317) lies at 151° . The curve for mixtures of *m*-dinitrobenzene and naphthalene falls to eutectic points at 50.3° and 50.5° for mixtures containing 60 and 42 molecular per cent. of naphthalene; the curve between the eutectic points is extremely flat, the maximum,

the melting of the easily dissociated additive compounds, lies at 50.8° ; such mixtures are termed by the author ψ -isomorphic. The curve for mixtures of nitrobenzene and naphthalene falls to one eutectic point at -6.8° for a mixture containing 14 molecular per cent. of naphthalene.

The curve for mixtures of *o*-nitrophenol and naphthalene has one eutectic point at 30° for a mixture containing 30 molecular per cent. of naphthalene.

The curve for mixtures of *p*-nitrophenol and naphthalene falls to a eutectic point at 73° for a mixture containing 77 molecular per cent. of naphthalene.

The curve for mixtures of *s*-trinitrobenzene and aniline has a eutectic point at 101° for a mixture containing 18 molecular per cent. of aniline, and another at -6° for a mixture containing 0.3—0.7 molecular per cent. of trinitrobenzene; the maximum at 125° represents an equimolecular mixture.

The curve for mixtures of *m*-dinitrobenzene and aniline falls from the melting point of dinitrobenzene to 40° , where there is a break, and then to a eutectic point at -8° for a mixture containing 4 molecular per cent. of *m*-dinitrobenzene; the break at 40° represents an additive compound containing 20 molecular per cent. of *m*-dinitrobenzene, which melts at 40° .

Mixtures of nitrobenzene and aniline give a curve which falls to a eutectic point at -29.8° for a mixture containing 41 molecular per cent. of nitrobenzene.

The curve for mixtures of trinitrotoluene and aniline falls to eutectic points at 60° and -8° for mixtures containing 85 and 1.5 molecular per cent. respectively of trinitrotoluene; the maximum between the eutectic points is 85° .

The curve for mixtures of dinitrotoluene and aniline falls in an almost straight line from the melting point of the former to a eutectic point at -13° for a mixture containing 11 molecular per cent. of dinitrotoluene.

The curve for mixtures of nitrotoluene and aniline has one eutectic point at -17° for a mixture containing 15 molecular per cent. of nitrotoluene.

G. Y.

Additive Compounds of Nitrosodimethylaniline. ROBERT KREMANN (*Monatsh.*, 1904, 25, 1311—1329. Compare foregoing abstracts).—Examination of the melting point curves for mixtures of nitrosodimethylaniline with *p*-toluidine, *o*-toluidine, *m*-xylidine, β -naphthylamine, and phenol shows that the following additive compounds are formed. The percentages are in molecular equivalents.

The additive compound with *p*-toluidine contains 66.6 per cent. of nitrosodimethylaniline; the eutectic points at 28° and 48.5° represent mixtures containing 27 and 33.4 per cent. of *p*-toluidine.

The additive compound with *o*-toluidine contains 66 per cent. of nitrosodimethylaniline, and melts at about 70° ; the eutectic points at 67° and below -18° represent mixtures containing 26 and over 95 per cent. of *o*-toluidine.

The additive compound with β -naphthylamine contains 60 per cent. of nitrosodimethylaniline and melts at 86° ; the eutectic points at 81°

and 75° represent mixtures containing 35 and 82 per cent. of nitrosodimethylaniline. The additive compound with phenol contains 66.6 per cent. of nitrosodimethylaniline and melts at 91°; the eutectic points at 24° and 74° represent mixtures containing 21 and 88 per cent. of nitrosodimethylaniline.

Two additive compounds are formed with *m*-xylydine; the one contains 60 per cent. of nitrosodimethylaniline and melts at 48°; the other contains 25 per cent. of nitrosodimethylaniline and melts at 26°; the eutectic points at 46.5°, 25°, and below -11° represent mixtures containing 63, 30, and about 2 per cent. of nitrosodimethylaniline.

The melting point curve for mixtures of nitrosobenzene and aniline falls to a eutectic point at -13° for a mixture containing 19 per cent. of aniline; no additive compound is formed. G. Y.

Polymerisation in the Liquid and Solid States. GEORGE G. LONGINESCU (*Ann. Sci. Univ. Jassy*, 1904, 3, 26—34. Compare Abstr., 1904, ii, 112; 1903, ii, 531).—Making use of the relationship $(T/C.D)^2 = n$, conclusions are drawn in regard to the state of aggregation of a number of organic substances containing bromine or iodine, of several organo-metallic compounds, and of various inorganic substances in the solid or liquid condition. The bromo- and iodo-derivatives and the organo-metallic compounds consist of simple molecules; this is also the case for the chlorides and bromides of arsenic and antimony, for chromyl chloride, germanium chloride, nickel carbonyl, lead tetrachloride, and selenium oxychloride. Other inorganic compounds, for example, lead chloride, lead bromide, and cadmium chloride, consist of very complex molecules, the association factor being greater than 50.

The value of *C* appears to be a function of the atomic weights of the constituent elements, and a method of ascertaining it is described.

The relationship is also applied to the elements, and the molecular complexity of 45 elements in the solid state and 13 in the liquid state is deduced. It would appear that carbon, silicon, lithium, and calcium contain more than 200 atoms in the molecule, glucinum, magnesium, and strontium more than 100. Sodium and potassium appear to be more highly polymerised in the liquid than in the solid state. Generally speaking, in any periodic group the degree of polymerisation decreases as the atomic weight increases. H. M. D.

Distribution of Soluble Substances between Water and Amyl Alcohol. WALTER HERZ and HERBERT FISCHER (*Ber.*, 1904, 37, 4746—4753).—Measurements are given of the constants of distribution between water and amyl alcohol of several acids and bases. In the case of the weaker acids (phenol and acetic acid), a constant value is obtained for all concentrations, but in the case of the stronger acids (succinic, oxalic, and picric acids) allowance has to be made for their degree of dissociation, a constant value for different concentrations being then obtained for the distribution of the undissociated substance. With the bases ammonia, methylamine, and triethylamine, the constant is independent of the concentration.

The distribution ratio of iodine between the two solvents is constant

for all concentrations. But with amyl alcohol and aqueous potassium iodide very different values are obtained for different concentrations, the ratio being also dependent on the nature of the potassium iodide solution.

W. A. D.

Determination of Molecular Weights in Solid Solutions.

FRIEDRICH W. KÜSTER [with WALTER WÜRFEL] (*Zeit. physikal. Chem.*, 1904, **50**, 65—80. Compare Abstr., 1894, ii, 274; 1895, ii, 439).—The freezing point curve for mixtures of *p*-dichloro- and *p*-dibromo-benzenes ascends regularly from the freezing point of the former to that of the latter, and is slightly convex to the concentration axis. The separating solid in each case is therefore an isomorphous mixture of the two constituents. The composition of the liquid phase in equilibrium with each isomorphous mixture may be deduced from its boiling point, for the boiling point curve of mixtures of the two substances is regular and somewhat similar in form to the freezing point curve. The solubility of the isomorphous mixtures in slightly diluted ethyl alcohol has also been determined, and these solubility experiments indicate that the molecules of the crystallised compounds are on the average greater than $C_6H_4Cl_2$ and $C_6H_4Br_2$, but smaller than $(C_6H_4Cl_2)_2$ and $(C_6H_4Br_2)_2$. The increase of solubility from the value for pure *p*-dibromobenzene is nearly proportional to the percentage of *p*-dichlorobenzene in the isomorphous mixture.

Mixtures of 2 : 4 : 6-trichlorophenol and 2 : 4 : 6-tribromophenol have been similarly investigated. The former compound is dimorphous, and the form which primarily separates on solidification is labile at the ordinary temperature. Tribromophenol does not exhibit dimorphism, and the form in which it separates on solidification is isomorphous with that form of trichlorophenol which is stable at the ordinary temperature. The freezing point of each compound is lowered by the addition of the other, and mixed crystals separate from the liquid mixtures; the mixed crystal series, however, exhibits a gap. The solubility of mixtures of the two substances in dilute methyl alcohol was studied. It is found that whilst the composition of the solutions changes regularly, the mixed crystals in equilibrium with the solutions undergo at one point an abrupt change both in appearance and in composition. When the concentrations of the chloro- and bromo-compounds in solution are plotted against the molecular concentration of the bromo-compound in the solid phase, two straight lines are obtained for each compound, corresponding with the labile and stable forms. The solubility of each form of trichlorophenol is proportional to its concentration in the solid phase, the solubility of the labile form being greater than that of the stable form. In the case of the mixed crystals containing labile tribromophenol, the solubility of the latter is proportional to its concentration in the solid phase, but on the other hand the solubility of the stable form of tribromophenol increases as its concentration in the solid phase diminishes. This peculiarity is probably due to an associating tendency on the part of tribromophenol, and this view is supported by determinations of the molecular weight in alcoholic solution.

J. C. F.

Stoichiometrical Laws and the Atomic Theory. LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1904, 975—983).—The author disagrees with Ostwald's view that, since the stoichiometrical laws are deducible from the principles of chemical dynamics, the atomic theory has become unnecessary for this purpose (*Trans.*, 1904, 85, 508).

T. A. H.

Lecture Experiments. [Liquid Ozone. Solid Nitrogen.] HUGO ERDMANN (*Ber.*, 1904, 37, 4739—4744).—An apparatus is described for storing and manipulating a solution of liquid ozone in liquid air: also another apparatus used for the preparation of solid nitrogen by rapidly boiling off the liquid gas, and suitable for demonstration on the lecture table.

E. F. A.

Bunsen Burner with Sieve Attachment. FELIX ALLIHN (*Chem. Zeit.*, 1905, 29, 34).—A piece of gauze is attached to the top of the ordinary Marshall burner, whereby a flame is obtained which is uniformly hot and especially suitable for heating platinum vessels.

A. McK.

Inorganic Chemistry.

Atomic Weight of Iodine. PAUL KÖTHNER and E. AEUER (*Annalen*, 1904, **337**, 123—169).—A preliminary account of this determination of the atomic weight of iodine has already been published (Abstr., 1904, ii, 556). In the present paper, the earlier work on this subject is discussed, more especially the recent work of Ladenburg. A detailed account of the methods employed in purifying the material and of the apparatus used in the various experiments is given. In discussing the results, it is pointed out that the new value for the atomic weight of iodine, 126.03 ($H=1$), agrees more closely with the values given by Ladenburg (126.008) and by Scott (126.01 and 126.03) than with Stas's mean value (125.90).
K. J. P. O.

Revision of the Atomic Weight of Iodine. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1904, **26**, 1577—1595).—Determinations of the atomic weight of iodine have been made by converting a known weight of pure silver into silver iodide. The silver was dissolved in nitric acid, and the solution was diluted with water and afterwards boiled to remove nitrous acid and nitrogen oxides. The solution was now treated with an excess of ammonia and afterwards with dilute solution of pure ammonium iodide prepared from highly purified iodine. Great precautions were taken in the purification of the materials and the collection of the silver iodide. Two samples of iodine were employed, one of which was collected in four fractions, the element being liberated from hydriodic acid by the action of potassium permanganate, which was

added in four successive quantities, distillation being carried out after each addition. The average result of 15 experiments gave the atomic weight of iodine 126.973 ($A_g = 107.930$), a result which is probably slightly too low. The very small differences in the results show that the samples of iodine were identical, and lead to the conclusion that no new halogen of higher atomic weight than iodine existed in the material employed in the investigation.

In another series of experiments, the ratio of silver to iodine was investigated by ascertaining the exact weight of silver required to combine with a weighed quantity of iodine. The average of three determinations gave the atomic weight of iodine 126.977.

In a third series of experiments, four determinations of the ratio of silver iodide to silver chloride were made by converting a weighed quantity of pure silver iodide into the chloride by heating it in a quartz crucible in a current of chlorine. Two determinations were made by heating silver iodide in a current of carbon dioxide and bromine and afterwards in chlorine. From the ratios obtained in these six experiments, the average atomic weight of iodine was found to be 126.975 ($A_g = 107.930$; $Cl = 35.467$; $O = 16$). The close agreement of this result with the average of the results of the first two series indicates that the atomic weight of iodine is 126.975, and is additional evidence in favour of the value 35.467 for the atomic weight of chlorine which was found by Richards and Wells in an investigation hitherto unpublished.

In connection with the experiments described in this paper, the sp. gr. of pure fused silver iodide was determined and found to be 5.674 at $25^{\circ}/4^{\circ}$.
E. G.

Flowers of Sulphur and Sublimed Sulphur. A. DOMERGUE (*Ann. Chim. anal.*, 1904, 9, 445—449).—According to the author, the name of *Flowers of sulphur* should be restricted to samples which, when newly made contain a minimum of 33 per cent. of sulphur insoluble in carbon disulphide. If containing less than this, the name sublimed sulphur should be applied.
L. DE K.

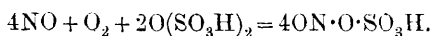
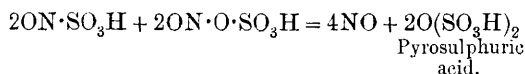
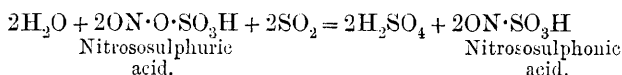
Contact Method for the Manufacture of Sulphuric Acid. FRIEDRICH W. KÜSTER [with FRANKE and GEIBEL] (*Zeit. anorg. Chem.*, 1904, 42, 453—469).—In order to maintain a uniform current of the mixture of sulphur dioxide and oxygen, the gases were passed from a copper gasholder, which is described in detail. Platinum, vanadium pentoxide, and ferric oxide induce for equal temperatures the same state of equilibrium between sulphur dioxide, oxygen, and sulphur trioxide. Platinum is the most effective of the three catalysts mentioned and is the only one of technical importance. Water has considerable influence on the catalytic activity of ferric oxide and vanadium pentoxide.

The catalytic effect of ferric oxide is impaired by its sensitiveness towards mechanical and chemical influences. The effect of increasing amounts of arsenious oxide on it is gradually to destroy its activity. Vanadium pentoxide is not, however, so sensitive in this respect.

A. McK.

Raschig's Theory of the Lead-chamber Process. EDWARD DIVERS (*J. Soc. Chem. Ind.*, 1904, 23, (24), 1178—1182).—The author gives a *résumé* of the facts adduced in support of the theories of Lunge and of Raschig and suggests a modification of Raschig's theory. According to this view, there is no significant quantity of any oxide of nitrogen in the actually gaseous part of the contents of the chamber in those regions where the change is in active operation, but nitrogen peroxide is present where the activity is much less. On entering the chamber from the Glover tower, the whole of the oxides of nitrogen together with sulphur dioxide and water condense to form a mist; sulphur dioxide, oxygen, and water then condense together upon the liquid particles of the mist and unite under the catalytic influence of the nitrous acid present in the particles.

In Raschig's theory of the chamber process, there is no place for nitrososulphuric acid, although, according to Lunge, its presence is certain and of prime importance. In the author's opinion, the nitrous acid in the liquid mist particles is present in the form of nitroso-sulphuric acid, which is to be looked on as a mixed anhydride of pyrosulphuric and nitrous acids, and the mechanism of the process can be expressed by writing nitroso-sulphuric acid for nitrous acid in Raschig's equations:



According to this, two molecules of sulphur dioxide and one molecule of oxygen are absorbed simultaneously by the liquid mist particles, and under the influence of the catalyser, which is supposed to be alternately nitrososulphuric acid and nitrososulphonic acid, sulphuric acid is continuously produced.

H. M. D.

Electrolytic Preparation of Persulphates. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE & ERICH MÜLLER (D.R.-P. 155805. Compare Müller and Friedberger, *Abstr.*, 1902, ii, 450; and Levi, *Abstr.*, 1903, ii, 474).—In the preparation of potassium persulphate by electrolysis without a diaphragm, the yield is greatly increased by the addition of hydrofluoric acid, becoming equal to that obtained in the preparation of ammonium persulphate. Potassium persulphate may thus be prepared directly, instead of by double decomposition from the ammonium salt. There is no loss of fluorine, and the anode remains bright throughout the process. In the electrolysis of ammonium sulphate, the yield of persulphate is not increased, but no evolution of nitrogen is observed. The influence of fluorine ions on electrolytic oxidation has been observed by Skirrow (*Abstr.*, 1903, ii, 69).

C. H. D.

Action of Hydrogen Sulphide on Selenious Acid. I. Sensitiveness of Selenium Sulphide towards Light. ALEXANDER GUTBIER and J. LOHMANN (*Zeit. anorg. Chem.*, 1904, **42**, 325—328).—When the yellow hydrosol, obtained by passing hydrogen sulphide into an aqueous solution of selenious acid, is boiled in presence of hydrochloric acid, a bright red precipitate is formed. This formation of the red hydrogel may also be induced by the influence of light. From the experiments described, it appears that the formation of red selenium sulphide is conditioned by the four factors, heat, time, light, and pressure. A. McK.

Reactions between Nitric Oxide and Oxygen or Atmospheric Air. GEORG LUNGE and E. BERL (*Chem. Zeit.*, 1904, **28**, 1243—1245).—The formation of nitric acid by the action of an excess of oxygen on nitric oxide is chiefly dependent on the amount of water present. With an optimum of the latter, nitric acid is formed in quantitative yield; with larger amounts of water, nitrous acid is formed in addition, and the more water is present the greater the amount of nitrous acid formed.

The presence of free nitrogen when atmospheric air is substituted for oxygen has no appreciable effect on the reaction, since nitric acid is also produced in this case in quantitative amount if the optimum quantity of water is present. The formation of nitric acid is a time-reaction. A. McK.

A Method for the Preparation of a Mixture of Nitric Oxide and Nitric Peroxide. J. MATUSCHEK (*Chem. Zeit.*, 1905, **29**, 31).—A mixture of nitric oxide and nitric peroxide is formed by the action of an aqueous solution of ferric chloride on sodium nitrite as represented by the equations: $\text{Fe}_2\text{Cl}_6 + 6\text{NaNO}_2 = \text{Fe}_2(\text{NO}_2)_6 + 6\text{NaCl}$ and $\text{Fe}_2(\text{NO}_2)_6 + 3\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_6 + 3\text{NO}_2 + 3\text{NO}$. Ferrous sulphate or ferric sulphate may be substituted for ferric chloride in the reaction. If sodium nitrite is placed under carbon disulphide and hydrated ferric chloride suspended in carbon disulphide is added, nitric oxide is alone evolved, the nitric peroxide remaining dissolved in the carbon disulphide. A. McK.

Theory of the Action of Metals on Nitric Acid. EDWARD DIVERS (*J. Soc. Chem. Ind.*, 1904, **23**, (24), 1182—1185. Compare Trans., 1883, **43**, 443; Veley, Abstr., 1891, i, 525; 1892, i, 410).—Silver and mercury only act on nitric acid in the presence of nitrous acid, which acts as catalyst, and molecular quantities of nitrite and nitrate are primarily produced according to the equation: $2\text{Ag} + 2\text{HNO}_3 = \text{AgNO}_2 + \text{AgNO}_3 + \text{H}_2\text{O}$. In this interaction, nitrous acid, nitrogen peroxide, and nitric oxide only appear as secondary products. The nitrous acid is formed by the action of nitric acid on the primary nitrite and the nitrogen peroxide by the interaction of the nitrous and nitric acids when the proportion of water is small. Nitric oxide results from the decomposition of nitrous acid when the proportion of water is large and that of nitric acid small.

The primary products of the action of zinc or tin on nitric acid are

zinc or stannous nitrate and either ammonia, nitrous oxide, or nitrogen, these three reduction products being produced independently of each other and without the formation of intermediate products. The primary formation of hydroxylamine only takes place if a stable acid, such as sulphuric or hydrochloric acid, is present. Nitrous acid or nitrite only appears as a secondary product, and nitric oxide and nitrogen peroxide are to be placed in the same category. The author thinks it possible to place all the metals in regard to their action on nitric acid in one of the above two classes. Bismuth and copper belong to the former, whilst all the strongly basic metals belong to the latter.

H. M. D.

Action of Carbon Dioxide on the Hydroxides and Carbonates of the Metals of the Alkalis and Alkaline Earths. PAUL N. RAIKOW (*Chem. Zeit.*, 1904, 28, 1247—1252).—Normal potassium carbonate in aqueous solution is completely converted into potassium hydrogen carbonate by an excess of carbon dioxide, no tetracarbonate being formed. The experiments made did not indicate the existence of the sesquicarbonate, $K_4H_2(CO_3)_3$.

When normal lithium carbonate is dissolved in water containing carbon dioxide, lithium hydrogen carbonate is probably formed; a little lithium tetracarbonate is probably also produced.

By the action of water containing carbon dioxide on normal sodium carbonate, the latter passes completely into the sodium hydrogen salt, the intermediate formation of sodium sesquicarbonate not having been observed. Similarly, in the formation of rubidium hydrogen carbonate from the normal salt, no tetracarbonate was formed; calcium, strontium, and barium carbonates respectively, under similar conditions, did not form tetracarbonates. Evidence is submitted to indicate the formation of hydrogen carbonates of lithium, calcium, strontium, and barium when an excess of carbon dioxide is passed into water containing the hydroxides or normal carbonates of those metals.

A. McK.

Affinity of Alkali Oxides towards Various Anhydrides. D. G. GERASSIMOFF (*Zeit. anorg. Chem.*, 1904, 42, 329—340).—The author has studied the action of sulphur trioxide on alkali tungstates and vanadates, respectively, and the action of carbon dioxide on the latter salts and also on alkali niobates, tantalates, titanates, and aluminates respectively. The avidity of alkali oxides towards carbon dioxide and sulphur trioxide respectively increases with the molecular weight of the alkali oxide. This is the case for all systems in which the following anhydrides take part:

CO_2 and SiO_2 (Wittorf), CO_2 and TiO_2 (Smith), CO_2 and WO_3 , CO_2 and V_2O_5 , SO_3 and WO_3 , SO_3 and V_2O_5 (the author).

By comparison of the relative affinity of the non-volatile anhydrides, it is found that in the systems where (a) sulphur trioxide and tungsten trioxide, and (b) sulphur trioxide and vanadium pentoxide are respectively concerned, vanadium pentoxide has a greater affinity than tungsten trioxide. When carbon dioxide competes with one of the anhydrides, V_2O_5 , Nb_2O_5 , SiO_2 , WO_3 , Al_2O_3 , TiO_2 , and Ta_2O_5 , the

sequence quoted represents the relative affinity of the latter anhydrides. The following indicates the number of molecules of carbon dioxide expelled by one molecule of the various anhydrides from two molecules of sodium carbonate at 880° , where the partial pressure of the carbon dioxide is 0.07 atmospheres: V_2O_5 , 2.000; Nb_2O_5 , 1.891; SiO_2 , 1.310; WO_3 , 1.047; Al_2O_3 , 1.019; TiO_2 , 0.779; Ta_2O_5 , 0.727. A. McK.

Dissociation of Ammonium Chloride in its Analytical Relations. LUIGI SANTI (*Chem. Centr.*, 1904, ii, 1625—1626; from *Boll. Chim. Farm.*, 43, 673—681).—Iron drillings are readily attacked by a hot concentrated solution of ammonium chloride with evolution of hydrogen and ammonia and yield the compound $FeCl_2 \cdot 2NH_4Cl$. Magnesium powder is attacked even in the cold, forming the double salt $MgCl_2 \cdot 2NH_4Cl$. Calcium, zinc, cerium, manganese, and tin are also more or less attacked. On heating cobalt and nickel oxides with dry ammonium chloride, they are reduced to the metallic state, but other oxides are converted into chlorides. On boiling calcium, nickel, manganous, and ferrous oxides with a solution of ammonium chloride, they are converted into chlorides with evolution of ammonia; sesquioxides, such as ferric oxide, are not attacked. Carbonates of calcium, magnesium, copper, cobalt, and nickel are also converted into chlorides with evolution of ammonium carbonate. The sulphides of tin and antimony are attacked by heating with dry ammonium chloride, whilst the sulphide of manganese, and in a less degree that of zinc, is attacked even by solutions of ammonium chloride. Sodium thio-sulphate solution, on boiling with ammonium chloride, is decomposed according to the equation $Na_2S_2O_3 + 2NH_4Cl = 2NaCl + H_2O + 2NH_3 + SO_2 + S$; if heated on a distilling apparatus, the distillate contains ammonium sulphide and polysulphide. Manganates are converted into permanganates, chromates into dichromates; the latter then even yield free chromic acid. Barium dioxide, when treated with ammonium chloride in the cold, yields hydrogen peroxide, but on heating there is an abundant formation of oxygen. Potassium persulphate yields chlorine and nitrogen and even hypochlorous acid. Glucosides (salicin, amygdalin) are practically unaffected by ammonium chloride.

L. DE K.

[Silver Dichromate.] OTTO MAYER (*Ber.*, 1904, 37, 4646).—A reply to Autenrieth's claim for priority (*Ber.*, 1904, 37, 3886).

W. A. D.

Certain Properties of the Alloys of Silver and Cadmium. T. KIRKE ROSE (*Proc. Roy. Soc.*, 1904, 74, 218—230).—The investigation consists in a determination of the temperatures of solidification of alloys of different composition, and in a study of their micro-structure. Evidence has been obtained of the existence of the compounds $AgCd_3$, Ag_2Cd_3 , $AgCd$, Ag_3Cd_2 , Ag_2Cd , and Ag_4Cd . The solid alloys containing from 0—25 per cent. of silver consist of crystals of $AgCd_3$ set in a matrix of cadmium. Those with 25—40 per cent. consist of the compound Ag_2Cd_3 set in a matrix which consists mainly of $AgCd_3$. The 50 per cent. alloy contains crystals of a substance rich

in silver set in a matrix consisting mainly of AgCd_3 . The matrix or eutectic solidifies at 420° , nearly 300° below the freezing point of the crystals. The alloys containing 50–60 per cent. of silver consist, above 420° , of mixtures of two different solid solutions, one composed chiefly of the compound AgCd and the other of Ag_3Cd_2 . Traces of the eutectic freezing at 420° are still visible. When more than 80 per cent. of silver is present, the alloys consist of a mixture of two substances at temperatures between the liquidus and solidus curves, but these unite to form a single solid solution at points on the solidus curve. The alloys containing over 80 per cent. of silver do not ordinarily undergo segregation, and are practically homogeneous and uniform in composition. They are well suited as a material for the manufacture of trial-plates. J. C. P.

Metallic Calcium. KURT ARNDT (*Ber.*, 1904, 37, 4733–4738. Compare Abstr., 1903, ii, 76).—Metallic calcium, prepared on a large scale by the electrolysis of fused calcium chloride, has been examined in detail by the author. The metal contains traces of silicon and aluminium as impurity, and when acted on by water yields almost pure hydrogen. The sp. gr. is 1.54, but rises to 1.56 on remelting owing to an increase in the percentage of silicon; when purified by distillation, the metal has a sp. gr. 1.52. Calcium melts at 800° and sublimates even below this temperature; the vapour reacts very vigorously with atmospheric air, and combines with oxygen and nitrogen even more readily than magnesium does. E. F. A.

Calcium Carbide as an Explosive in Mining Operations. MARCEL P. S. GUÉDRAS (*Compt. rend.*, 1904, 139, 1225–1226).—An explosive mixture of acetylene and air obtained by the action of water on calcium carbide in a limited space, and fired by means of an electric spark, can be used for blasting operations in mining, and the author describes a cartridge containing an air chamber and charged with calcium carbide (50 grams) and water separated by a membrane, which can be mechanically pierced after the cartridge is placed in the bore-hole; after five minutes, the acetylene (15 litres) mixed with the air is fired electrically. M. A. W.

Preparation of Barium. ANTOINE GUNTZ (*Ann. Chim. Phys.*, 1905, [viii], 4, 5–25).—A *résumé* of work already published (compare Abstr., 1901, ii, 385; 1902, ii, 138; 1903, ii, 369, 410).—The purest specimen of the metal obtained contained 98.35 per cent. of barium, melted at about 850° , and boiled at about 1150° . M. A. W.

Decomposition of Barium Nitrate by Heat. E. BASCH (*Chem. Zeit.*, 1905, 29, 31).—The author corroborates Gottlieb's results (Abstr., 1904, ii, 403). A. McK.

Decomposition of Alkaline Earth Carbonates by Alkali Chlorides in Presence of Water. H. CANTONI and G. GOGUÉLIA (*Bull. Soc. chim.*, 1905, [iii], 33, 13–27. Compare Abstr., 1904, ii, 334).—The influence of temperature, time, and concentration on the rate of

decomposition of barium carbonate by solutions of potassium and sodium chlorides has been investigated, and some further observations have been made on the action of sodium, potassium, and ammonium chlorides on alkaline earth carbonates at the ordinary temperature over comparatively long periods. The results, which are tabulated and graphically represented in the original, show that under all conditions the action of potassium chloride on barium carbonate is initially greater than that of sodium chloride, and increases more rapidly with increase of concentration, rise of temperature, and lapse of time, although the last factor exerts less influence than the two former in differentiating the action of the two chlorides. At the ordinary temperature, the activity of the three chlorides diminishes in the following order: ammonium, potassium, sodium; whilst the resistance of the three alkaline earth carbonates towards all three chlorides increases in the order: barium, calcium, strontium. Solutions of sodium or potassium chloride have practically no action on strontium carbonate.

T. A. H.

Silicates. IV. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1904, 42, 418—432. Compare Abstr., 1903, ii, 475, 542, 595).—Details are given of the preparation and analysis of the silicates of the alkaline earths previously described.

In concentrated barium hydroxide solutions, the metasilicate, $\text{BaSiO}_3 \cdot \text{H}_2\text{O}$, is formed. By the action of strontium hydroxide on metasilicic acid, a compound was obtained containing $2/3\text{SrO} : 1\text{SiO}_2$; another preparation contained the proportion $1/3\text{SrO} : 1\text{SiO}_2$.

By the action of calcium hydroxide on silicic acid, the metasilicate was not formed, but a compound containing $2/3\text{CaO} : 1\text{SiO}_2$.

The reaction between silicic acid and calcium hydroxide in presence of $1/1$ mol. calcium chloride solution was studied. Mixtures were obtained.

The authors were unable to confirm the results of Wahl (Abstr., 1902, ii, 501), who claims to have obtained the silicate $\text{BaSiO}_3 \cdot 6\text{H}_2\text{O}$ by the action of barium hydroxide on quartz.

A. McK.

Separation of Glucinum from Aluminium and Iron. G. VAN OORDT (D.R.-P. 155466).—The salts of glucinum with fatty acids dissolve in chloroform (Lacombe, Abstr., 1902, ii, 122). Glucinum may be separated from aluminium and iron by converting the mixed salts into acetates, digesting with glacial acetic acid, and extracting with chloroform, in which the pure glucinum acetate only dissolves. The treatment with glacial acetic acid is necessary in order to convert the insoluble acetate into the crystalline form, soluble in chloroform. A solution of glucinum hydroxide in hydrochloric acid is quite colourless when free from iron.

C. H. D.

Salts and Substances for Incandescent Lighting. HANS BUNTE (*Chem. Centr.*, 1904, ii, 1627—1628; from *J. Gasbel.*, 47, 1011—1013).—Since Eitner has found that the temperature of the Bunsen flame is itself considerably higher (1390 — 1545°) than that of

the mantle at corresponding points (1265—1395°), the temperature of the latter cannot be appreciably affected by a catalytic action of the incandescent mass. According to Schmidt, the light emitted by pure thorium oxide becomes of a bluer tint as the temperature rises, whilst the nature of the light from cerium oxide is the same at all temperatures of the flame. When the proportion of cerium oxide to thorium oxide is gradually increased to 0.5 per cent., the luminosity of the mantle becomes greater, and the light of a bluer tint. Further addition of cerium oxide up to 1.5 per cent. still increases the luminosity, but the light now appears to be tinged with red. The illuminating power is decreased by larger proportions of cerium oxide, and the character of the light approaches more and more to that emitted by the pure oxide. The first effect of rise of temperature is to increase the blue rays, but when the light has attained a great intensity, all the rays are affected in practically the same way. It has been found that when mantles of different weights but of the same composition are employed, the light obtained from the heavier mantles is not so blue as that emitted by the lighter. The high temperature of the cerium oxide in the flame is partly due to its state of division and partly to the small amount present, whilst the lighting effect is primarily the result of selective radiation.

E. W. W.

The Element Z₈. P. É. LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1904, **139**, 1015—1016).—Contrary to the statement of Urbain (compare this vol., ii, 35), the author maintains that the elementary nature of Z₈ was fully established by him in 1895 (compare Abstr., 1896, ii, 249), although he did not succeed in obtaining the element free from dysprosium.

M. A. W.

Basic Alumino-silicates containing Haloids. Z. WEYBERG (*Centr. Min.*, 1904, 729—734).—By fusing kaolin with calcium chloride, Gorgeu (Abstr., 1888, 228) obtained tetrahedra of the compound $3\text{SiO}_2, 3\text{Al}_2\text{O}_3, 6\text{CaO}, 2\text{CaCl}_2$. This result is confirmed, and by fusing kaolin with calcium bromide, tetrahedra with the composition $5\text{SiO}_2, 8\text{Al}_2\text{O}_3, 12\text{CaO}, 4\text{CaBr}_2$ were obtained. In both cases, prismatic crystals of another alumino-silicate were also formed. Kaolin, when fused with a small amount of calcium bromide, gave tetragonal prisms with the composition $\text{SiO}_2, \text{Al}_2\text{O}_3, 2\text{CaO}$.

L. J. S.

Products of Weathering of Silicates in Clay, Volcanic and Laterite Soils respectively. JAKOB M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1904, **42**, 265—314. Compare Abstr., 1902, ii, 70).—In soils where the products of weathering contain much alumina relatively to silica, all determinations of silica made by extracting it with hydrochloric acid are without value, since the extraction is incomplete. If, however, the soil, after treatment with hydrochloric acid, is agitated for several minutes with dilute sodium or potassium hydroxide at about 50°, the residual silicic acid is dissolved.

The ratio of alumina to silica as determined in a large number of the products of weathering of alluvial plastic clays, soils of volcanic origin, and laterite soils respectively was not constant. In ordinary

alluvial clays, the portion extracted from the disintegrated silicate by hydrochloric or by sulphuric acid indicated that the weathering had taken place in a single stage, whilst with the volcanic and laterite soils examined, various stages of weathering were recognisable, the products consisting of a mixture of silicates. The progress of the weathering was best exhibited with the laterites, the final product being in those cases hydrargillite.

The metals of the alkalis and of the alkaline earths are also present in varying amounts in the products of weathering examined, but not in sufficient amount to conclude that chemical compounds were present of the composition $m(\text{SiO}_2), n(\text{Al}_2\text{O}_3), o(\text{MO}), p(\text{H}_2\text{O})$, where m, n, o , and p are whole numbers. The amount of those bases present diminishes the further the weathering has proceeded.

Estimations of the amount of water in air-dried clays showed that ordinary clays contain very little water, which is lost at 15° when the clay is exposed to an atmosphere dried with concentrated sulphuric acid. They contain about $2\text{H}_2\text{O}$, which is lost at a higher temperature. The laterites examined contained more than $2\text{H}_2\text{O}$.

The more basic the products of weathering are, the more readily do they dissolve in hydrochloric acid.

The amount of iron oxide in various soils was also determined. This iron oxide generally contains at the ordinary temperature a little more than $1\text{H}_2\text{O}$ and at 100° rather under $1\text{H}_2\text{O}$.

The constitution of the silicates obtained by the weathering of clays and the process of weathering itself are discussed.

Tables of the various analyses made are appended. A. McK.

Absorption of Water by Clay. JAKOB M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1904, 42, 314—324).—Various soils were dried at 100° and the percentage of water absorbed at 15° under varying vapour pressures was estimated. The process of absorption is reversible; the hydration and dehydration can be repeated as often as desired, and the amount of hysteresis varies with the amount of absorption.

Determinations of the rate at which the water absorbed was expelled show that it was not essentially different from the rate at which water itself evaporates under similar conditions. A. McK.

Reduction of Manganese Oxides by Amorphous Boron. Preparation of a New Manganese Boride. BINET DU JASSONNEIX (*Compt. rend.*, 1904, 139, 1209—1211).—Manganese oxides are readily reduced when heated with boron in an electric furnace for a few seconds with a current of 400 amperes and 100 volts; if excess of boron is used, the product consists of a mixture of manganese and a new manganese boride, MnB (compare Troost and Hauteville, *Abstr.*, 1876, i, 883), which can be isolated in the form of a crystalline powder, having a sp. gr. 6.2 at 15° , by the limited action of chlorine on the mixture at a dull red heat. Manganese boride burns in fluorine at the ordinary temperature, is attacked by chlorine or bromine at a red heat, whilst the action of iodine at a high temperature is only superficial; it forms a fusible borate when heated in oxygen, is not attacked by nitrogen; it slowly decomposes, cold water forming manganic hydroxide and boric acid;

dissolves in dilute hydrochloric acid, and is attacked by hydrogen chloride or hydrogen fluoride, nitric or sulphuric acids; by the action of ammonia at 1000° , a compound is obtained which contains nitrogen, is not attacked by acids, and yields manganates with evolution of ammonia on fusion with alkali carbonates. M. A. W.

Composition of the Four Sulphides of Manganese. JOHN C. OLSEN and W. S. RAPALJE (*J. Amer. Chem. Soc.*, 1904, **26**, 1615—1622).—An investigation of the sulphides of manganese has shown that three sulphides exist, two of which, the red and the green, are anhydrous, whilst the grey sulphide contains a large proportion of water.

The pink sulphide of manganese obtained by the action of ammonium sulphide on a neutral solution of manganous chloride appears to be a mixture of the grey and red sulphides in varying proportions. The pink sulphide is not uniform in composition, and contains from 4 to 14 per cent. of free sulphur and a varying amount of water. When heated at 360° in an atmosphere of hydrogen, it is gradually converted into the green modification.

When precipitation is effected with colourless sodium sulphide, a brick red sulphide of fairly constant composition is obtained, containing about 0.75 per cent. of water. On heating the pink sulphide with hydrogen sulphide, the product obtained consists of lumps which are grey on one side and red on the other. The reason that the sulphide precipitated by sodium sulphide cannot be converted into the green modification, whilst that produced by ammonium sulphide readily undergoes this change, is probably that the latter product contains varying amounts of the grey sulphide.

The green modification is the most stable form of the sulphide, is more distinctly crystalline than the other forms, and is probably more complex in structure. E. G.

Influence of Water Vapour on the Reduction of the Oxides of Iron by Mixtures of Carbon Monoxide and Carbon Dioxide. OCTAVE BOUDOUARD (*Compt. rend.*, 1905, **140**, 40—42).—Comparative measurements of the reduction of ferric oxide by gaseous mixtures containing equal volumes of carbon monoxide and carbon dioxide have been made, the gas being dried in one series of experiments, and saturated with water vapour at room temperature in another. The gas was passed over the ferric oxide contained in a porcelain boat, which was heated in an electric resistance furnace maintained at constant temperature, each experiment lasting one hour. The following numbers give the percentage loss of weight of the ferric oxide:

Temperature	400°	550°	800°	925°	1050°
Dry gas	0.87	4.3	4.0	5.6	6.5
Moist gas	0.45	3.8	2.65	4.4	6.9

The reduction effected by the dry gas is considerably greater at the lower temperatures, but there appears to be little difference in the action at about 1000° . Similar data were obtained in experiments on

the reducing action of dry and moist carbon monoxide on ferrous oxide at 850° .

The author considers that the results are in harmony with the increased economy which accompanies the use of dry air in the blast furnace.
H. M. D.

Formation and Solubility of Double Chlorides of Iron and the Alkali Metals. F. WILLY HINRICHSSEN and EUGEN SACHSEL (*Zeit. physikal. Chem.*, 1904, 50, 81—99).—Determinations of solubility and dilatometric investigation show that in the case of sodium and ferric chlorides there is no formation of double salt between 0° and 60° . At 21° , potassium and ferric chlorides form a double salt of the composition $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$; if, however, the potassium chloride is in excess, mixed crystals are formed (compare Roozeboom, *Abstr.*, 1892, 1384). The temperature at which the double salt is formed from the separate salts is 22.0 — 22.5° . No evidence could be found for the existence of the double salt, $\text{FeCl}_3 \cdot 3\text{KCl}$, referred to by Werner. In the case of caesium and ferric chlorides at 21° , two double salts are stable: (1) a yellow salt, $\text{FeCl}_3 \cdot 3\text{CsCl} \cdot \text{H}_2\text{O}$, produced when the solution contains excess of caesium chloride, (2) a red salt, $\text{FeCl}_3 \cdot 2\text{CsCl} \cdot \text{H}_2\text{O}$, formed in presence of excess of ferric chloride at 39.5 — 39.8° . The authors were unable to isolate the compound $\text{FeCl}_3 \cdot \text{CsCl} \cdot \frac{1}{2}\text{H}_2\text{O}$ described by Walden (*Abstr.*, 1895, ii, 165).

The compounds $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 2\text{CsCl} \cdot \text{H}_2\text{O}$ are in harmony with Werner's views regarding the "co-ordination number" (see *Abstr.*, 1902, ii, 554). The other caesium double salt, $\text{FeCl}_3 \cdot 3\text{CsCl} \cdot \text{H}_2\text{O}$, is not in harmony with these views.

Incidentally, the solubility of caesium chloride has been determined at several temperatures between 0° and 40° .
J. C. P.

Preparation of Iron Phosphide from Calcium Phosphate. GUSTAVE GIN (D.R.-P. 156087).—Iron phosphide may be prepared in a closed electric furnace from calcium phosphate and iron, silica being added as a flux. Iron pyrites may be employed as a reducing agent instead of the carbon hitherto used: $4\text{Ca}_3\text{P}_2\text{O}_8 + 12\text{SiO}_2 + 5\text{FeS}_2 + 11\text{Fe} = 8\text{Fe}_2\text{P} + 12\text{CaSiO}_3 + 10\text{SO}_2$; or $5\text{Ca}_3\text{P}_2\text{O}_8 + 15\text{SiO}_2 + 10\text{FeS}_2 + 5\text{Fe}_2\text{O}_3 = 10\text{Fe}_2\text{P} + 15\text{CaSiO}_3 + 20\text{SO}_2$.

The temperature required is slightly above the melting point of iron. Several arcs, each with a tension of 25 to 30 volts, enter the same crucible, and the energy consumed amounts to 50—60 volts per sq. cm. of electrode surface. Acid calcium phosphates may be employed to economise flux. Some free phosphorus is formed by secondary reactions, and is absorbed in a chamber containing iron borings.

C. H. D.

Alloys of Cobalt and Nickel. W. GUERTLER and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1904, 42, 353—362).—The authors have studied the melting-point curve of alloys of cobalt and nickel to determine whether a compound of these metals is formed, or whether both metals separate completely or incompletely from the molten mass.

When cobalt is heated, it is, like nickel, converted into a stable, non-magnetic variety.

In the curve represented, where the abscissæ indicate the composition of the mixture and the ordinates the melting points observed, the melting-point curve is represented by a straight line, the course of which is expressed by the formula $\Delta t_0 = 0.35p$, where p indicates the percentage of cobalt and Δt_0 the rise of melting point. The variation of each individual melting point from this straight line amounts to only $\pm 5^\circ$. Nickel and cobalt accordingly separate from their molten masses in mixed crystals.

Cobalt is transformed into the non-magnetic variety at 1150° , whereas nickel is transformed at 323° . The equilibrium curve of the magnetic and non-magnetic crystal forms of nickel, cobalt, and their alloys was studied. The transition temperature of alloys containing 10 per cent. of cobalt rises from 100° to 60° , from which the conclusion is drawn that the concentration of the single crops of mixed crystals, which separate from the same molten mass, cannot differ from one another by more than 2 to 3 per cent. Various mixtures of nickel and cobalt were taken and the lowest temperature determined at which those mixtures became non-magnetic; the temperatures were also noted at which the mixtures again became magnetic after having been cooled.

The melting point of gold is 1044° .

In the concentration-temperature diagram sketched in the paper, the melting-point curve separates the field of the molten mass from the field of non-magnetic crystals, whilst the transition curve separates the latter from the field of magnetic crystals. At the temperatures of the melting-point curve, from the melting point of pure nickel, 1484° , to the melting point of pure cobalt, 1528° , the composition of the molten mass and of the mixed crystals which separate is approximately identical. At the temperatures of the transition curve, the magnetic mixed crystals are in equilibrium with the non-magnetic mixed crystals.

A. McK.

Triamminecobalt Salts. A New Case of Hydrate Isomerism.

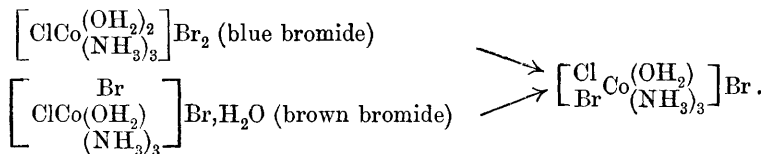
ALFRED WERNER and ADOLF GRÜN (*Ber.*, 1904, **37**, 4700—4706).—*Chlorodiaquatriamminecobalt nitrate*, $[\text{CoCl}(\text{OH}_2)_2(\text{NH}_3)_3] \cdot \text{NO}_3$, formed by the addition of a freshly-prepared solution of chlorodiaquotriamminecobalt chloride to nitric acid of sp. gr. 1.4, separates in bluish-violet needles. The corresponding *bromide*, $\text{CoCl}(\text{OH}_2)_2(\text{NH}_3)_3\text{Br}_2$, prepared by the addition of the chloride to hydrobromic acid of sp. gr. 1.49, crystallises in dark blue needles. It is very unstable, and in a moist atmosphere forms *chlorobromoquatriamminecobalt bromide*, $[\text{CoClBr}(\text{OH}_2)(\text{NH}_3)_3]\text{Br}$, a green salt from which the original bromide may be regenerated in small amount by suspending it in alcohol and gradually adding water.

The solution of chlorodiaquotriamminecobalt bromide in water is blue, and when heated becomes red. When hydrobromic acid is added to the blue solution, the isomeric *chlorobromoquatriamminecobalt bromide*, $[\text{CoClBr}(\text{OH}_2)(\text{NH}_3)_3]\text{Br} \cdot \text{H}_2\text{O}$, separates in brown needles, even at temperatures below 0° . It is more stable than the blue iso-

meride, and is converted into the green chlorobromo-aquotriamminecobalt sulphate by the action of concentrated sulphuric acid. It may also be prepared by the action of hydrobromic acid on dichloro-aquotriamminecobalt chloride, when it separates in glistening, chocolate-coloured leaflets. Below 0° it forms a green solution with water, at the ordinary temperature a bluish violet, and at higher temperatures a red solution.

When chlorodiaquotriamminecobalt sulphate is triturated with fuming hydrobromic acid, anhydrous chlorobromo-aquotriamminecobalt bromide separates in olive-green crystals.

The structural relationship between the three bromides described is expressed as follows:

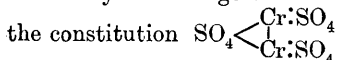


A. McK.

Existence of a Normal Green Chromic Sulphate. ALBERT COLSON (*Compt. rend.*, 1905, 140, 42—44).—When the green solution obtained by reducing chromic acid by means of sulphur dioxide at 0° is completely evaporated in a vacuum, an amorphous, green, hygroscopic substance of the composition $\text{Cr}_2(\text{SO}_4)_3 \cdot 10\text{H}_2\text{O}$ is obtained. The substance appears to be a normal chromium sulphate; its aqueous solutions do not contain free sulphuric acid, and the green colour of the solutions is permanent. On addition of barium chloride, a considerable proportion of sulphuric acid is precipitated. It differs from the green sulphate described by Recoura (*Abstr.*, 1892, i, 411), for the green colour of solutions of this soon changes to violet, and barium sulphate is not precipitated on addition of barium chloride.

On boiling the aqueous solution, a change takes place which is represented by the equation $2\text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{Cr}_4\text{O}(\text{SO}_4)_5 + \text{H}_2\text{SO}_4$.

The density of the solution is smaller after boiling, and the heat development, on addition of barium hydroxide, indicates the presence of one molecule of free acid in the boiled solution for every two molecules of the original salt. The freezing point of the solution is unaltered by the change which takes place. The salt is supposed to have



H. M. D.

Uranyl Selenide and Potassium Chromic Selenide. JAR. MILBAUER (*Zeit. anorg. Chem.*, 1904, 42, 450—452).—*Uranyl selenide*, UO_2Se , prepared by heating a mixture of selenium, potassium cyanide, and uranium oxide (prepared from uranyl acetate) at a low red heat, forms black, hexagonal prisms with a metallic lustre and closely resembling uranyl sulphide. When cold hydrochloric acid is added to it, hydrogen selenide is evolved and uranyl chloride produced. It is acted on very vigorously by nitric acid, selenium at first separating and then gradually oxidising.

Potassium chromic selenide, $K_2Cr_2Se_4$, prepared by heating a mixture of selenium, potassium cyanide, and chromium sesquioxide at a red heat, forms dark green, hexagonal crystals, which are readily soluble in nitric acid, but insoluble in hydrochloric acid. A. McK.

Action of Sodium Hyposulphite on Metallic Salts. II. OTTO BRUNCK (*Annalen*, 1904, **336**, 281—298. Compare Abstr., 1903, ii, 481).—On addition of a solution of sodium hyposulphite to solutions of metallic salts, mostly one of three reactions takes place: (a) the precipitation of a sulphide, (b) reduction to the salt of a lower oxide, or (c) complete reduction to the metal.

The following reactions with sodium hyposulphite are described.

Thallium salts, at the ordinary temperature, and indium salts, on boiling, yield the sulphides, but incompletely owing to the action of sulphurous acid formed. In a neutral solution, stannous chloride forms a precipitate of stannous hyposulphite, which dissolves in an excess of the reagent, but in presence of an excess of acid, stannous sulphide is formed; solutions of stannic chloride are completely precipitated as the sulphide. In neutral solutions, lead salts are completely precipitated as the yellow hyposulphite which changes into the black sulphide. Molybdic acid forms the sulphide in neutral solutions, whilst tungstic is reduced in slightly acid solution. Nickel and cobalt salts form the sulphides quantitatively in neutral, ammoniacal, or weak acetic acid solutions.

Titanium tetrachloride is reduced in neutral solution to the trichloride, but not in alkaline solution, as the action is reversed; similarly, chromates are reduced to chromium oxide, permanganates to manganese salts, ferric to ferrous salts, and, on heating, to ferrous sulphide, and platinic to platinous chloride with precipitation of sulphur.

Salts of palladium, selenates, and tellurates are reduced in neutral solutions completely to palladium, selenium, and tellurium respectively. Similarly, arsenic is obtained from its oxygen compounds as a brown powder which, if the reduction takes place in a strongly acid solution, contains arsenic trisulphide and sulphur.

The behaviour of salts of antimony and of bismuth is similar to that of the salts of copper.

Solutions of salts of germanium are apparently unaffected at the ordinary temperature, but, on warming, sulphur is precipitated.

G. Y.

Inactive Thorium. CHARLES BASKERVILLE and FRITZ ZERBAN (*J. Amer. Chem. Soc.*, 1904, **26**, 1642—1644).—It has been shown by Hofmann and Zerban (Abstr., 1903, ii, 732) that inactive thorium can be obtained from certain minerals which do not contain any radioactive constituent.

A new source of inactive thorium has been found in a rock from South America, which is of a greyish-slate colour, consists chiefly of barium carbonate containing a very small percentage of thorium, and exhibits no radioactivity. E. G.

Decomposition of Antimony Hydride. ALFRED STOCK (*Zeit. physikal. Chem.*, 1904, 50, 111—112).—A continuation of a discussion with Bodenstein (see Bodenstein, *Abstr.*, 1904, ii, 245, 719; Stock and Guttman, *ibid.*, 489).
J. C. P.

Purification of Tantalum. SIEMENS & HALSKE AKTIENGES. (D.R.-P. 155548).—Crude tantalum, obtained by reduction with sodium, always contains oxide, which may be removed by fusion in a closed exhausted electric furnace. The crude tantalum, compressed into a crucible of thoria or magnesia, forms the anode; the cathode consists of a rod of pure tantalum or silver, which is movable from the outside of the enclosing vessel. An arc is started, and is then caused to travel over the whole anode surface, when fusion to a homogeneous, non-porous mass occurs.
C. H. D.

Mineralogical Chemistry.

Jordanite from Upper Silesia. ARTHUR SACHS (*Centr. Min.*, 1904, 723—725).—A massive mineral, which forms with galena and blende a vein in grey dolomite in the Blei-Scharley mine at Beuthen, is proved by the following analysis to be jordanite ($\text{Pb}_4\text{As}_2\text{S}_7$):

Pb.	S.	As.	Fe.	Total.
70.19	18.21	11.37	0.19	99.96

The bearing of the discovery of this arsenical mineral on the origin of the ore-deposits at Beuthen is discussed. L. J. S.

Minerals from Arizona. WALDEMAR LINDGREN and WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1904, [iv], 18, 448—460).—The minerals described are from the copper deposits at Clifton and Morenci. The principal ore is massive chalcocite, which has resulted from the replacement of pyrites by means of descending solutions of cupric sulphate. A partial analysis of the chalcocite gave 96 per cent. Cu_2S and 2.4 per cent. FeS_2 , the latter probably mechanically admixed.

Coronadite.—A black metallic mineral, not unlike psilomelane in general appearance, and intimately intermixed with quartz, is found in fairly large amount in the Coronado vein; it is named coronadite. It has a finely fibrous structure; hardness about 4; streak, black with a brownish tinge. Analysis gave:

MnO_2 .	MnO .	PbO .	ZnO .	CuO .	MoO_3 .	Al_2O_3 .
56.13	6.56	26.48	0.10	0.05	0.34	0.63*
Fe_2O_3 .	H_2O .	Insol. and SiO_2 .		$\text{CaO, MgO, Alk., \&c.}$	Total.	Sp. gr.
1.01	1.03	7.22		0.45	100.00	5.246

* With a little TiO_2 , P_2O_5 , V_2O_5 .

These results give the formula $R''O, 3MnO_2$, or, considered as a salt of a derivative of ortho-manganous acid, $R''(Mn_3O_7)''$. Taking into account the water (only 0.14 per cent. of which is lost below 200°), the formula would be $R_4''H_2(Mn_{12}O_{29})$; the water is, however, probably due to incipient alteration.

Chrysocolla is of common occurrence in the oxidised part of the deposits, and shows, as usual, variations in composition. Microscopical examination shows that the different concentric layers have different microcrystalline structures. The term *chrysocolla* probably includes two mineral species.

Copper-pitch-ore.—This occurs in association with the *chrysocolla*. It is a dark brown to black substance, with sometimes a dull, but generally a glassy to resinous, lustre. In thin sections it is opaque or translucent, the latter being optically isotropic. A partial analysis gave :

CuO.	ZnO.	MnO.	Fe ₂ O ₃ , Al ₂ O ₃ , P ₂ O ₅ .	Insol. in HCl (SiO ₂).	Loss on ignition.	Total.
28.6	8.4	21.2	4.0	22.8	13.7*	98.7

Copper-pitch-ore is usually considered to be impure *chrysocolla*, but the material now described contains no *chrysocolla*, and it does not appear to be a mixture. It is in some respects related to *melanochalcite* (Abstr., 1903, ii, 156).

Morencite.—This name is given to a mineral which occurs in calcareous shale at Morenci as brown or green spreading masses. It is rendered impure by intermixed chlorite and pyrites, but more pure material is present as brownish-yellow, silky, fibrous seams intersecting the mass. Under the microscope, the minute fibres are brownish-yellow and slightly pleochroic, and extinguish parallel to their length. Analysis gave :

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.
45.74	trace	1.98	29.68	0.83	trace	1.61	3.99
K ₂ O.	Na ₂ O.	H ₂ O (105°).	H ₂ O (>105°).	CuO.	FeS ₂ .	P ₂ O ₅ .	Total.
0.20	0.10	8.84	5.08	little	0.66	0.18	98.89

Neglecting water, a metasilicate formula, $R_2''R_6'''(SiO_3)_{11}$, is derived, whilst with the water as essential the ratio is that of an orthosilicate. The substance is optically well individualised, and is evidently an alteration product of some metasilicate contact-metamorphic mineral.

Other minerals described from this district are : willemite, hemimorphite, diophtase, libethenite, and bronchantite, all of which are found as distinct crystals; also the rare minerals spangolite ($H_{18}Cu_6AlClSO_{19}$) and gerhardtite ($H_6Cu_4N_2O_{12}$). Microscopical examination of the green ores proves that bronchantite is of extremely common occurrence, mostly intergrown with malachite.

L. J. S.

Emmonsite (?) from a New Locality. WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1904, [iv], 18, 433—434).—A green mammillary

* Less O due to conversion of MnO_2 to Mn_3O_4 .

mineral occurring with gold and tellurite at Cripple Creek, Colorado, and resembling durdenite in appearance was found, on analysis, to approximate to emmonsite in composition. The cleavage and optical characters are also in general agreement with those previously described for emmonsite. The following results (22.44 per cent. gangue, mainly quartz, deducted) give the ratios $\text{TeO}_2 : \text{Fe}_2\text{O}_3 : \text{H}_2\text{O} = 3.16 : 1.00 : 1.77$.

TeO_2 .	Se.	Fe_2O_3 .	H_2O at 100° .	H_2O above 100° .
70.71	nil	22.76	0.21	4.54
P_2O_5 .	Al_2O_3 .	SiO_2 , &c.	Total.	Sp. gr.
0.34	0.56	0.88	100.00	4.53

L. J. S.

The Sodalite Series. Z. WEYBERG (*Centr. Min.*, 1904, 727—729).
 —This is a continuation of the work of Lemberg, Thugutt (Abstr., 1895, ii, 358), and Morozewicz (Abstr., 1899, ii, 764) on derivatives of the group $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$. A mixture of silica, alumina, and soda in the proportions $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ was fused with sodium chromate; there was obtained a yellow, crystalline powder of isotropic grains and cubes with the composition $7\text{SiO}_2, 4\text{Al}_2\text{O}_3, 5\text{Na}_2\text{O}, \text{CrO}_3$
 ($= 7\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8, \text{Na}_2\text{Al}_2\text{O}_4, 2\text{Na}_2\text{CrO}_4$).

L. J. S.

Physiological Chemistry.

Changes in the Viscosity of the Blood produced by Alcohol. RUSSELL BURTON-OPITZ (*J. Physiol.*, 1904, 32, 8—17).—The viscosity values were obtained by Hürthle's method. The addition of 0·7 per cent. solution of sodium chloride to blood causes an immediate and distinct decrease of viscosity, whilst equal amounts of distilled water render the blood slightly more viscous. Alcohol intravenously injected or absorbed from the alimentary canal increases the viscosity of the blood; the effect lasts from 30 to 45 minutes. The sp. gr. and viscosity vary in the same manner. The experiments were made on dogs.
W. D. H.

Nuclei of Birds' Red Corpuscles. D. ACKERMANN (*Zeit. physiol. Chem.*, 1904, 43, 299—304).—A mass of nuclei of the birds' red corpuscles was obtained by a method of washing with saline solution, then with water to remove hæmoglobin, and centrifugalising. Lecithin and cholesterol were removed by alcohol, and phosphorus and nitrogen estimated in the residue; from the numbers obtained, it is calculated that the nuclei consist of 42 per cent. of nucleic acid and 58 per cent. of histon.
W. D. H.

Gaseous Metabolism of the Kidney. JOSEPH BARCROFT and THOMAS G. BRODIE (*J. Physiol.*, 1904, 32, 18—27).—The experiments were made on dogs which had been subjected to evisceration, an operation they survive about eight hours. Diuresis, usually produced by injection of urea, is accompanied by a large increase of oxygen absorption in the kidney, but that increase is not in proportion to the diuresis produced. In only one experiment was there any increase in the carbon dioxide given out. There is no definite relation between the oxygen absorbed and the carbon dioxide given out at any one time. The volume of the latter is often in excess of the former, especially at the commencement of an experiment, before diuresis has been set up. The amount of the two gases exchanged during diuresis varies from 0.002 to 0.281 c.c. per gram of kidney substance per minute. There is no necessary accompaniment of increase of blood flow, and this is never in proportion to the acceleration of the urine flow. The blood gases were estimated by the pump and by the Barcroft-Haldane method. W. D. H.

Nutritive Value of Proteid Decomposition Products. I. W. CRONHEIM (*Pflüger's Archiv*, 1904, 106, 17—42).—The experiments were made on men and dogs, and compare the work of the digestive tract during feeding on flesh and somatose. The latter can be given in large quantities (30 grams) to men without producing intestinal irritation; this quantity necessitates a smaller digestive activity than flesh containing an equivalent amount of nitrogen. W. D. H.

Sulphur and Phosphorus Metabolism on an Abundant Proteid Diet. KARL BORNSTEIN (*Pflüger's Archiv*, 1904, 106, 66—79).—The higher the percentage of neutral phosphorus and sulphur in the urine, the smaller is the oxidative power of the organism. The experiments recorded lend support to the doctrine that an abundant proteid diet improves the cellular activities of the organism. W. D. H.

Peptic Digestion Products of Plasteins. JOSEPH GROSSMANN (*Beitr. chem. Physiol. Path.*, 1905, 6, 191—205).—The addition of a peptic digest of plasteins to the finely subdivided mucous membrane of stomach or intestine (obtained from fed or hungry dogs) leads at 38° to 40° to a disappearance of non-coagulable and a corresponding appearance of coagulable proteid material. This is a proof that the mucous membrane contains not only proteolytic enzymes, but agents which act in the opposite direction. W. D. H.

Formation of Sugar from Proteid. HUGO LÜTHJE (*Pflüger's Archiv*, 1904, 106, 160—167).—The pancreas was removed from a dog and the animal observed for about a month, during which time it was kept on a proteid diet (mainly nutrose); the total sugar in the urine was far too large to be accounted for by that in the food, or present as glycogen in the body: the remainder must therefore have been derived from proteid. W. D. H.

Pancreatic Diabetes. EDUARD PFLÜGER (*Pflüger's Archiv*, 1904, 106, 168—172).—A commentary on Luthje's work (see preceding abstract), in which it is shown that a large amount of the excreted sugar cannot have had a carbohydrate origin; the figures work out rather differently from those calculated by Luthje, but the main conclusion is corroborated. The author holds that the sugar excreted as the result of feeding on proteids (and the same is true for feeding on alanine, glycine, asparagine, &c.) is due to an indirect action, analogous to the way in which ammonium carbonate will cause an increase in the hepatic glycogen, and, further, that the sugar attributed to proteid decomposition really originates from fat. In many diabetics there is no increased nitrogen excretion. W. D. H.

Are Proteolytic and Rennetic Ferments Identical? IVAR BANG (*Zeit. physiol. Chem.*, 1904, 43, 358—360).—Pawloff has advanced the view that the rennet action of gastric juice is a property of pepsin, and holds similar views regarding other rennetic ferments. In the present communication, a number of weighty arguments are adduced to show that this cannot be the case. W. D. H.

The Lymph-flow from the Pancreas. F. A. BAINBRIDGE (*Brit. Med. J.*, 1904, ii, 1742—1744; *J. Physiol.*, 1904, 32, 1—8).—The intravascular injection of secretin or extract of ileum in dogs causes an increased flow of lymph from the thoracic duct. This has also been shown to be the case by Falloise (*Bull. Acad. Roy. Belg.*, 1902, No. 12, p. 945). After ligation of the portal lymphatics, secretin still causes an increased flow of lymph, whereas ileum extract has no effect. The increased flow of lymph is closely related to the secretion of pancreatic juice; it is derived entirely from the pancreas, and is probably formed as a result of metabolic changes occurring in the pancreas during the secretion of the juice. It is produced by secretin, and not by the depressor substance in the extract. W. D. H.

Influence of Alkalis on the Growth of Bone. HANS ARON (*Pflüger's Archiv*, 1904, 106, 91—92).—A preliminary account of experiments to show the importance of sodium and potassium salts in the food on the growth of bone. W. D. H.

Condition of Water in the Tissues. R. DU BOIS REYMOND (*Chem. Centr.*, 1904, ii, 1661—1662; from *Verh. Ges. Deut. Nf. Ärzte*, 1903, II, (2), 437—440).—The swelling which certain tissues undergo with water is regarded not as due to mechanical forces, but more probably to chemical union. This is supported by experiments with dried albumin. W. D. H.

Universal Presence of Erepsin in Animal Tissues. HORACE M. VERNON (*J. Physiol.*, 1904, 32, 33—50).—Erepsin was obtained in glycerol extracts of a large number of tissues of both vertebrate and invertebrate animals; least was obtained from invertebrates, and most from mammals. The kidney is richest in the enzyme; then follow intestinal mucous membrane, pancreas, spleen, and liver; then after a

large drop, heart muscle; whilst skeletal muscle and brain tissue are poorest. The relative amount in the tissues is constant and not a matter of chance, and must be related to their function. The lower the animal in the scale of evolution, the less are its tissue erepsins influenced by the reaction of medium; in mammals, an alkaline medium is most and an acid medium least efficacious. To some extent the tissue erepsins are specific, the intestinal extract, for instance, having relatively much more action on partially hydrolysed peptones than kidney and liver extracts.

W. D. H.

Chemical Changes produced in Flesh by Fungi. P. W. BUTJAGIN (*Arch. Hygiene*, 1905, 52, 1—21).—During the development of *Penicillium glaucum* and *Aspergillus niger* in flesh, the amount of water increases, the absolute amount of nitrogen diminishes, and the nitrogenous compounds soluble in water increase; the ethereal extract is lessened, especially in early stages, and the amount of extractives increases; the alkalinity rises, as also does the amount of volatile acids. The fungi appear to secrete enzymes which are proteolytic and lipolytic. Some quantitative differences between the actions of the two fungi are noted, and on the whole *P. glaucum* destroys the constituents of flesh more rapidly.

W. D. H.

Tyrosinase in the Skins of some Pigmented Vertebrates. FLORENCE M. DURHAM (*Proc. Roy. Soc.*, 1904, 74, 310—313).—An aqueous extract of the skins of rabbits, rats, guinea-pigs, and chickens acts on tyrosine and produces a pigmented substance. This suggests the presence of a tyrosinase in the skins of these animals. The action takes place most readily at 37° and is destroyed by boiling; the presence of an activating substance like ferrous sulphate is necessary to start it. Black substances are obtained when animals with black pigment in their skins are used, and yellow substances when the skin contains the yellow pigment. These coloured substances are soluble in alkalis, but insoluble in acids.

W. D. H.

Fat in Milk. WILHELM CASPARI (*Chem. Centr.*, 1904, ii, 1664—1665; from *Zeit. Biol.*, 46, 277—279).—Polemical. The question raised is the origin of the milk fat from the fat of the food. The casein used by some observers was not absolutely free from fat. Iodocasein and iodoalbumin freed from fat cause no trace of iodised fat in the milk.

W. D. H.

Functions of Thyroid and Parathyroid Glands. SWALE VINCENT and W. A. JOLLY (*J. Physiol.*, 1904, 32, 65—86).—Removal of both thyroid and parathyroid does not necessarily cause death; but fatal results, when they do occur, are due to the absence of these glands. Great variations obtain in the animal kingdom in this matter. Rats and guinea-pigs do not suffer at all. Monkeys show transient nervous symptoms. Dogs and cats suffer severely and usually die. In foxes, the symptoms are of rapid onset, and death occurs early. No symptoms of myxœdema were ever observed; this disease is therefore due to causes more complex than thyroid insufficiency. In young

animals, however, thyroid extirpation causes temporary cessation of growth. When the thyroid is removed, the parathyroids appear capable of replacing it to some extent, and their histological structure changes accordingly.

W. D. H.

Elimination of Urea in Healthy Subjects. HENRI LABBÉ and E. MORCHOISNE (*Compt. rend.*, 1904, 139, 941—943).—That the amount of urea depends on the amount of proteid ingested is supported by the experiments recorded on a number of healthy people on the same diet. The amount in all was approximately identical.

W. D. H.

Organic Phosphorus in Urine. DOUGLAS SYMMERS (*J. Pathol. Bacteriol.*, 1905, 10, 159—172).—The estimation of inorganic phosphates is not a true index of phosphorus metabolism; in various pathological conditions, the phosphoric acid in organic combination may be frequently 25—50 per cent. of the total. The excretion of organic phosphorus is to a certain extent rhythmical. The amount is pronounced in lymphatic leucæmia, and especially in degenerative nervous diseases. It may be due to an increase in endogenous phosphorised katabolites, or may be an expression of lessened oxidation which normally would give inorganic phosphates as the end-products. The theory that it originates from bone is dismissed, for in extensive disease of bone like osteomalacia the output of phosphoric acid is not increased.

W. D. H.

Substances Soluble in Ether in Human Fæces. FELIX OEFELE (*Chem. Centr.*, 1904, ii, 1664; from *Ber. Deut. pharm. Ges.*, 14, 355—371).—Analytical numbers are given for preformed neutral fat, fatty acids, lecithin, &c., in the fæces. A part is unsaponifiable. Great variations occur in health.

W. D. H.

Pernicious Anæmia. G. LOVELL GULLAND and ALEXANDER GOODALL (*J. Pathol. Bacteriol.*, 1905, 10, 125—144).—This is a megaloblastic anæmia; the blood cells are abnormally vulnerable; a toxin is produced which does not always originate in the intestine. The large red corpuscles produced in the marrow fall a ready prey to endothelial cells and leucocytes. In some cases this is congenital. The accumulation of iron in the liver is the usual result of excessive blood destruction, and does not necessarily mean that the actual destruction occurs altogether in that organ.

W. D. H.

Acid Dyscrasia. ALEXANDRE DESGREZ and J. ADLER (*Compt. rend.*, 1904, 139, 944—945. Compare *Abstr.*, 1904, ii, 193).—An acid dyscrasia can be produced in guinea-pigs by repeated subcutaneous injections of hydrochloric acid. In this condition, there are (1) a preponderating disintegration of the proteids rich in sulphur, (2) a lessening of the urine formed, and (3) a considerable increase of nitrogenous metabolites in the tissues. The conditions are similar to those noted in skin diseases.

W. D. H.

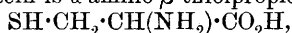
Influence of Fever on the Reducing Action of the Organism. C. A. HERTER (*Amer. J. Physiol.*, 1904, 12, 457—465).—The temperature of rabbits was raised either by superheating or infection with hog-cholera. Elevation of temperature accelerates the reduction of methylene-blue by various types of cells. The differences of colour are especially striking in brain, skeletal muscles, heart, spleen, pancreas, and liver. A method for measuring the reaction-velocity of reduction was also devised.

W. D. H.

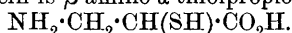
Production and Inhibition of Glycosuria in Rabbits by Salts. MARTIN H. FISCHER (*Pflüger's Archiv*, 1904, 106, 80—83).—Intravenous injection of sodium chloride and other sodium salts in rabbits produces glycosuria, which is inhibited by calcium chloride. This is most readily produced if the injection is made towards the brain; the salt probably produces an osmotic change which affects the "diabetes centre." Cutting the splanchnic nerves prevents it. Lithium, strontium, and potassium salts also produce similar glycosuria; ammonium salts do so also in large doses, but here hæmoglobinuria also occurs. Calcium and magnesium salts kill the animal before any sugar can pass into the urine. Non-electrolytes such as urea, alcohol, and glycerol are inactive.

W. D. H.

Cystinuria. I. ADOLF LOEWY and CARL NEUBERG (*Zeit. physiol. Chem.*, 1904, 43, 338—354).—Friedmann and Neuberg have shown that the cystin of urinary calculi (calculus-cystein) is not identical, but isomeric, with that obtained from the decomposition of horn (protein-cystin). Protein-cystein is α -amino- β -thiolpropionic acid,



whereas calculus-cystein is β -amino- α -thiolpropionic acid,



The special interest of this isomerism arises from the fact that this is one of the rare instances of a β -amino-acid arising during animal metabolism. Tryptophan is another instance (indole- β -aminopropionic acid, Ellinger), and some of Levene's amino-acids do not belong to the α -series. A patient æt. 18, excreting 0.5 gram of cystin daily, came under the authors' notice, and, contrary to expectation, this was protein-cystin. Acting on the supposition that the case was not merely one of anomalous proteid metabolism, but one in which there was a general breakdown of amino-acid metabolism, the urine was searched for other amino-acids, but without success; diamines were also absent. The anomalous nature of the metabolism was, however, shown when amino-acids were administered by the mouth. Tyrosine, leucine, and aspartic acid, instead of being broken down in the body, were excreted in the urine almost quantitatively; the same was true for protein-cystin (given in 6-gram doses), whereas a normal man will burn 8 grams with the formation of sulphates and thiosulphates. On the other hand, calculus-cystin was completely burnt with a corresponding increase in sulphates and neutral sulphur. After feeding on lysine, cadaverine (pentamethylenediamine) appeared in the urine, and putrescine (tetramethylenediamine) appeared after the administration of arginine. There is here a direct fermentative splitting off of carbon dioxide, the first time

it has been shown to occur *in vivo*. Whether this is brought about by enzymes or by intestinal bacteria it is impossible to say, for the patient would not permit subcutaneous injections, but the discovery of arginine by Kossel and Dakin would appear to point to an enzyme, for ornithine, by loss of carbon dioxide, would yield tetramethylenediamine.

The interest of the case is this: if proteids are normally broken up in the alimentary canal into simple crystalline cleavage products, why did not this patient excrete them unchanged, as he did when they were given by the mouth? This tells against the theory of complete proteolytic breakdown in the intestine. It may be that cystin is specially loosely combined in the proteid molecule. Further experiments with polypeptides, proteoses, and peptones are in progress.

W. D. H.

Oxaluria. FRIEDRICH KUTSCHER and MARTIN SCHENK (*Zeit. physiol. Chem.*, 1904, 43, 337).—By oxidation of gelatin with calcium permanganate, important amounts of oxamic acid are obtained. The mother substance of this must be glycine. Proteids poor in the glycine radicle, such as casein and pseudomucin, yield little or none. On the clinical side, Lommel (*Deutsch. Arch. klin. Med.*, 1899) showed that feeding with gelatin produced oxaluria. Oxidation in the body doubtless caused the appearance of oxamic acid, and this is broken down with the formation of oxalic acid and ammonia.

W. D. H.

Elimination of Sulphur and Phosphorus, Demineralisation of the Organism, and Size of the Molecule Elaborated in Skin Diseases. ALEXANDRE DESGREZ and J. AYRIGNAC (*Compt. rend.*, 1904, 139, 900—901).—The examination of the urine in cases of skin disease shows that the disintegration is most marked in those proteids which are rich in sulphur. What is termed demineralisation of the organism was higher than normal in 56 per cent. of the cases.

W. D. H.

Tetanus and Quinine. E. VINCENT (*Ann. Inst. Pasteur*, 1904, 18, 748—760).—Observers have not infrequently described tetanus as a sequel to injections of quinine given for malaria. In these days of antiseptics, this cannot be due to infection from dirty instruments. Quinine hydrochloride kills the tetanus bacillus, and so cannot favour its development. The fatal dose of quinine varies a good deal in different animals; this had to be determined before the next experiments were performed; these consisted in subcutaneously administering quinine either with or subsequently to a subcutaneous dose of tetanus bacilli, and the remarkable fact was elicited that these animals quickly died, whereas those who received only one of the two substances injected recovered. With the injection of both, the bacilli multiply more rapidly and pass more into other tissues. Quinine given by other channels does not act thus. Its action is attributed to its harmful action on leucocytes. If quinine is given subcutaneously for malaria, and the patient has cutaneous excoriations, it is wise to administer also antitetanic serum.

W. D. H.

Action of Chloroform on the Heart and Arteries. EDWARD A. SCHÄFER and HERBERT J. J. SCHARLIEB (*Trans. Roy. Soc. Edin.*, 1904, 41, Part II, (No. 12), 311—341. Compare Abstr., 1903, ii, 437).—By perfusing the vessels of a frog with blood or saline solution containing a high percentage of chloroform (1 to 5 grams per litre), the blood-vessels are directly constricted; with more dilute mixtures, the effect is less pronounced, but dilatation is never obtained. In experiments on mammals, the same main effect is produced, even with dilute solutions, except in the kidney, where the vessels are dilated. The effect is one on muscular tissue, not on vaso-motor nerve-endings, for apocodeine does not abolish the effect, as it does that of adrenaline. The fall of blood pressure seen is of cardiac origin, the depressant effect on the heart being more than sufficient to counterbalance constriction of peripheral vessels. The effect on the heart resembles that of vagus excitation, except that the arrest is more permanent. With the arrest of the circulation, the respiratory centre also fails secondarily. During light anaesthesia, vagus excitation easily causes arrest of the heart, which, however, soon escapes from vagus control, but in deep anaesthesia the effect is more pronounced.

Quite small doses of atropine (0·00002 gram per kilo. of body weight in the dog given subcutaneously) prevent the effect of vagus excitation on the heart, and this lasts for three hours. The precaution of administering a dose of atropine before chloroform anaesthesia in man should never be omitted, even although it will not prevent death when an overdose of chloroform produces paralysis of respiration and complete “paralytic dilatation” of the heart. The cardiac arrest sometimes noticed in the initial stage of anaesthesia is a reflex vagus effect; this is prevented by atropine. The paralytic dilatation that occurs in later stages when too much chloroform is given is due to action in the neuro-muscular inhibitory end-apparatus rather than in the muscle itself. The heart is then entirely inexcitable, and respiration fails first. This final effect on the heart is not antagonised by atropine, nor is adrenaline of any avail as a rule. The addition of small quantities of ammonia vapour or ammoniated alcohol to the chloroform inhaled in cases where danger is signalled is strikingly beneficial, and alcohol vapour itself without the ammonia is nearly as good. The alcohol in A.C.E. mixture is needlessly excessive. The post-mortem appearances after death from chloroform inhalation are very similar to those seen in asphyxia due to deprivation of air, or by drowning, even although there may be no true asphyxia and a free supply of air by artificial perfusion.

W. D. H.

Action of Monatomic Alcohols on Simple Organs. PAUL GRÜTZNER and H. BREYER (*Chem. Centr.*, 1904, ii, 1665; from *Verh. Ges. Deut. Ntf. Ärzte*, 1903, II, (2), 443).—These alcohols act harmfully on cilia, the higher ones more intensely and rapidly.

W. D. H.

Relations between the Chemical Constitution and Physiological Action of some Ammonium Bases. ERNST SCHMIDT (*Arch. Pharm.*, 1904, 242, 705—714. Compare especially Abstr., 1892, 905, and this vol., i, 23; also, for the preparation of the substances in

question, Abstr., 1892, 806, 949, 950; 1894, i, 433; 1901, i, 443; this vol., i, 23).—A *résumé* of matter already published. C. F. B.

Betaine. ALOIS VELICH (*Zeit. Zuckerind. Böhm.*, 1904, 29, 14—25).—The author finds that pure betaine has no poisonous action, the effects noticed by Waller and Lowton (Abstr., 1904, ii, 65) being due to the insufficient neutralisation of the betaine hydrochloride employed. Even after very strong doses, the author is unable to find any diminution of the blood pressure or retardation of the pulse.

T. H. P.

Effect of Adrenaline on Excretion of Sugar and Nitrogen in Birds. DIARMID NOËL PATON (*J. Physiol.*, 1904, 32, 59—64).—When adrenaline is administered subcutaneously, it produces glycosuria in birds as in mammals. It does not act through the pancreas. It causes a decrease in the proportion of nitrogen elaborated into uric acid, an increase of the nitrogen present as ammonia, and probably in that in urea also.

W. D. H.

Selective Action of Cocaine on Nerve-fibres. WALTER E. DIXON (*J. Physiol.*, 1904, 32, 87—94).—Cocaine locally applied to nerve-fibres picks out and paralyses some before others: sensory before motor, afferent before efferent vagal fibres, vaso-constrictors before vaso-dilators, and broncho-constrictors before broncho-dilators.

It is suggested that the local application of cocaine to the vagi may be a means of combating death during early chloroform narcosis. Drugs which attack the central nervous system almost invariably attack the sensory cells and fibres before the motor. There is no reason to suppose that cocaine has a specific action on sensory nerve-endings.

W. D. H.

Physiological Action of Azoimide. LETCHWORTH SMITH and C. G. L. WOLF (*J. Medical Research*, 1904, 12, 451—474).—Azoimide is a very powerful protoplasmic poison; the effect of small doses is almost instantaneous death. It is almost impossible to determine the details of its action, unless very small doses are employed, and the use of the sodium compound minimises to some extent the danger and unpleasant symptoms which the observers experience. The experiments made on frogs and mammals show that the action in the main resembles that of hydrocyanic acid. Muscle and nerve are simultaneously paralysed after a preliminary stage of increased excitability. The respiratory centre is similarly first excited, and then paralysed. The fall of blood pressure seen is primarily due to vascular dilatation, especially in viscera other than intestine and kidney. It forms a compound with methæmoglobin resembling that formed by hydrocyanic acid, but the existence of a compound with hæmatin or hæmoglobin was not made out. Introduction of a phenyl radicle lessens its action.

W. D. H.

The Toxic and Anti-toxic Action of Salts. ALBERT P. MATHEWS (*Amer. J. Physiol.*, 1904, 12, 419—443).—The valence of an

ion is of little or no importance in determining its anti-toxic action. Attention should therefore be directed to its other properties, potential weight, velocity, and volume.

W. D. H.

Action of Calcium Permanganate on Alkaloids. G. BAUDRAN (*Compt. rend.*, 1904, 139, 1000—1002).—If strychnine sulphate or hydrochloride is treated at 37° with a 5 per cent. solution of calcium permanganate, a product is obtained which, when mixed with strychnine, annihilates its poisonous effects. Similar results were obtained with morphine and aconitine. The products all contain manganese.

W. D. H.

Chemical Combination and Toxic Action as Exemplified in Hæmolytic Sera. ROBERT MUIR and CARL H. BROWNING (*Proc. Roy. Soc.*, 1904, 74, 298—309).—In the action of a complement there are two distinct factors: (1) the power of chemical combination, and (2) toxic action, which correspond to Ehrlich's haptophore and zymotoxic groups. Deficiency in action does not necessarily imply absence of the first factor, but may be due to the non-sensitiveness of the tissue molecule to the second group. In testing the corpuscles of an animal, it is found that very large doses of both complement and immune-substance are necessary if serum from the same species of animal is used, and want of sensitiveness is especially noticeable in connection with the zymotoxic group. In some cases there is also deficiency in the combining power of the complement with the receptors of red corpuscles. The differences of dosage of the immune-substance with different complements, and also of various complements, do not appear to be due to multiplicity of immune-substances.

W. D. H.

Plurality of Cytolysins in Snake Venom. SIMON FLEXNER and HIDEYO NOGUCHI (*J. Pathol. Bacteriol.*, 1905, 10, 111—124).—Snake venoms from different sources contain solvents for numerous cells other than blood corpuscles. This is due to a number of distinct solvents, and depends on the interaction of amboceptors and complements. The latter are contained within the affected cell.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

New Method for the Purification of Water Supplies.
GEORGE T. MOORE (*Amer. J. Pharm.*, 1904, **76**, 553—564).—The treatment consists in adding copper sulphate to the water in the proportion of 1 to 5,000,000. By this means, the growth of algæ is prevented, sewage bacteria are destroyed, and the total number of bacteria is reduced by at least 95 per cent. Over 50 public water supplies in the United States are now being treated with copper sulphate, the reservoirs concerned holding from a few to hundreds of

millions of gallons. The quantity of copper added to the water is considered to be too small to have the slightest effect on the health of the consumers, even if copper itself be injurious, which is doubtful.

W. P. S.

The Copper Treatment of Water. HENRY KRAEMER (*Amer. J. Pharm.*, 1904, 76, 574—579).—The results are given of experiments carried out for the purpose of testing the efficiency of copper in reducing the number of micro-organisms in drinking-water. The conclusions arrived at are : (1) that intestinal bacteria, such as *Bacillus coli* and *B. typhosus*, are completely destroyed by placing clean copper-foil in the water containing them ; (2) that the effects of colloidal copper and copper sulphate in the purification of drinking-water are, in a quantitative sense, much like filtration, only the organisms are completely destroyed ; (3) that, pending the introduction of the copper treatment on a large scale, drinking-water may be purified by the use of strips of copper foil, 3·5 inches square to each quart of water ; after being allowed to act for 8 hours at the ordinary temperature, the water is then drawn off or the strips are removed.

W. P. S.

Hydrogen Sulphide Microbes in Mineral Waters. N. GOSLINGS (*Centr. Bakt. Par.*, 1904, ii, 13, 385—394).—Passugger water was found to contain sulphate-reducing bacteria, perhaps Beijerinck's *Microspira desulfuricans* ; but attempts to obtain pure cultures of the hydrogen sulphide microbe were unsuccessful.

N. H. J. M.

Is Hydrogen Peroxide suitable for Sterilising Milk ? P. GORDAN (*Centr. Bakt. Par.*, 1904, ii, 13, 716—728).—Small amounts of hydrogen peroxide, as employed by Budde (*Milch-Zeit.*, 1903, No. 44), have practically no sterilising action on milk. Larger quantities, which impart an unpleasant taste to the milk, have a temporarily retarding effect on the growth of the bacteria. Complete sterilisation is only effected by amounts three times as great as those employed by Budde, and the milk is then useless for human consumption. The process is, besides, troublesome and rather expensive. N. H. J. M.

Production of Fat from Proteid by *Bacillus pyocyaneus*. S. P. BEEBE and B. H. BUXTON (*Amer. J. Physiol.*, 1904, 12, 466—470).—In growths of *Bacillus pyocyaneus* in proteid media, a pellicle of fat is formed ; this is partly crystalline, and various constants were determined. It is probable that the fat is formed in part by oxidation of albumoses apart from any carbohydrate nucleus they may contain.

W. D. H.

Respiration and Fermentation of Mould Fungi in Rose Cultures. T. KRASNOSSELSKY (*Centr. Bakt. Par.*, 1904, ii, 13, 673—687).—*Mucor spinosus* and *Aspergillus niger* give in air, on substrata capable or incapable of fermentation, similar curves of elimination of carbon dioxide. In absence of oxygen they behave

differently on fermentable substrata, the carbon dioxide curve showing that fermentation takes place with *Mucor spinosus*, but not with *Aspergillus*.

Mucor spinosus, on non-fermenting substrata, and *Aspergillus*, on both substrata, give off less carbon dioxide in hydrogen than in air. Sometimes only traces of carbon dioxide are produced. Under these conditions, they can live a long time (67 and 141 hours respectively), and become capable of further development when air is admitted. The amount of carbon dioxide then rapidly increases and may often exceed the amount produced under normal conditions of aëration. This vigorous production of carbon dioxide does not, however, last long. The results are similar to those observed by Palladin with *Chlorothecium saccharophilum*.
N. H. J. M.

Comparative Production of Alcohol and Carbon Dioxide during Fermentation. LÉON LINDET and P. MARSAIS (*Compt. rend.*, 1904, 139, 1223—1225).—It has been established by Pasteur, by Gay-Lussac, and by Buchner and Hahn that the ratio between the alcohol and carbon dioxide in the final products of fermentation is sensibly equal to unity; the authors find, however, that if the alcohol and carbon dioxide are estimated during the process of fermentation, the ratio, which is greater than unity at the early stages of the process, diminishes towards unity as the reaction proceeds. The experiments were conducted on three equal quantities of sterilised grape extract containing the same quantities of the same yeast, and the alcohol and carbon dioxide estimated at three different stages of the reaction. Further experiments showed that the ratio between the alcohol and carbon dioxide is not appreciably influenced by changes in the temperature or in the acidity of the sucrose extract. The initial preponderance of the alcohol over the carbon dioxide is connected with the growth of the yeast, which is more rapid at the early stages of the fermentation.

M. A. W.

The Alcoholic Ferment of Yeast Juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Physiol. Soc.*, Nov., 1904, 1—2; *J. Physiol.*, 32).—The alcoholic fermentation of dextrose by yeast juice is greatly increased (doubled) by the addition of boiled and filtered yeast juice, although the latter fluid is itself incapable of causing the fermentation. This may be due to an increase in the activity of the alcoholic ferment or to a decrease in that of the proteolytic enzyme (endotryptase); the former, however, is the more important action of the two. The substance in the boiled juice responsible for this action, or “co-ferment,” is not affected by boiling; it is dialysable and precipitated by 75 per cent. alcohol. By filtration through a gelatin filter, the enzyme and its co-ferment can be separated; neither by itself produces fermentation; a mixture of the two is equal in power to the original juice. No co-ferment of endotryptase was discovered.

W. D. H.

Nitrification and Denitrification in Arable Soil. F. LÖHNIS (*Centr. Bakt. Par.*, 1904, ii, 13, 706—715).—Denitrification in soils can only be inconsiderable owing to the amount of air present. Pro-

duction of proteids is also inconsiderable owing to the absence, as a rule, of sufficient readily assimilable organic matter. Nitrification generally greatly exceeds the antagonistic processes, because the conditions usually present in soils are more favourable to nitrifying organisms than to the others. All three processes may, however, under certain conditions be going on simultaneously.

N. H. J. M.

Assimilation of Free Nitrogen by Bacteria. GEORGE S. FRAPS (*Rep. of Chemist, Agric. Exper. Stat. N.C.*, 1902—1903, 40—44).—The results of preliminary experiments on soil bacteria which assimilate free nitrogen without symbiosis indicated that the greatest activity is in alkaline solutions containing glucose (2), potassium phosphate (0.2), sodium chloride (0.2), magnesium sulphate (0.2), and ferric chloride (0.01 per cent.), calcium carbonate (0.5 per cent.) being present. Less activity was observed when magnesium sulphate was omitted, and much less in neutral solutions containing mannitol, potassium sulphate, ferric chloride, and soil.

Bacteria may possibly exist which are more active in a neutral medium. Substitution of glucose by starch did not increase the assimilation of nitrogen. Nearly all the nitrogen was fixed in the first week of the experiment, a small amount being fixed in the second week.

N. H. J. M.

Nitrification of Different Fertilisers. W. A. WITHERS and GEORGE S. FRAPS (*Rep. of Chemist, Agric. Exper. Stat. N.C.*, 1902—1903, 3—8).—Four soils, a poor sandy soil, a rich loamy soil, a rich clay soil, and a poor clay soil (500 grams of each), in jars, received calcium carbonate (5.1 grams) and 0.3 gram of nitrogen in the form to be tested. The jars were kept at a temperature of about 35° and water was added twice a week so as to maintain an amount equal to about one-third of the saturation capacity. After four weeks, the amount of nitrogen as nitrates was determined.

Nitrification varied somewhat in the different soils. Taking the amount of cotton-seed nitrified as 100 in each case, the variations were as follows: ammonium sulphate, 13 to 127; dried blood, 70 to 120; fish, 85 to 100; bone, 22 to 43.

In the case of farm-yard manure (16.1 grams to 500 grams of soil) there was less nitrification in three of the soils than occurred without manure, whilst in the fourth soil (the poor clay) 0.5 per cent. of the nitrogen was nitrified.

N. H. J. M.

Studies on Nitrification. GEORGE S. FRAPS (*Rep. of Chemist, Agric. Exper. Stat. N.C.*, 1902—1903, 9—30).—The number of nitrifying organisms in a soil varies according to conditions of moisture and temperature, &c., and their activity is periodic, rapid nitrification being preceded and followed by periods of less activity.

Soils contain two groups of nitrifying organisms, one which nitrifies cotton-seed meal, the other ammonium sulphate. The relative numbers of one group may be increased by growing in a soil containing the corresponding manure.

There are probably four groups of organisms, three which successively convert organic nitrogen into ammonium salts, nitrites and nitrates, and one which directly produces nitrites or nitrates from organic nitrogen.

Ammonium sulphate is nitrified more quickly than the phosphate, chloride, or citrate.
N. H. J. M.

Nitrification of Ammonia fixed by Chabazite. W. A. WITHERS and GEORGE S. FRAPS (*Rep. of Chemist, Agric. Exper. Stat. N.C.*, 1902—1903, 31—32).—Chabazite (250 grams) was kept for two days in a solution of ammonium chloride (40 grams in 1 litre). After being washed, it contained 1.26 per cent. of nitrogen. An amount containing 0.3 gram of nitrogen was added, with calcium carbonate (5.1 grams), to 500 grams of soil which were kept for 3 weeks at 35°. It was found that the ammonia absorbed by the chabazite was much more readily nitrified than ammonium sulphate, or cotton-seed meal, added directly to the soil. It is possible, therefore, that zeolitic silicates in soils may assist the nitrification of ammonium sulphate by fixing a portion of the salt.
N. H. J. M.

Nitrifying Power of Typical North Carolina Soils. W. A. WITHERS and GEORGE S. FRAPS (*Rep. of Chemist, Agric. Exper. Stat. N.C.*, 1902—1903, 33—39).—The nitrifying power of fifteen soils varied from 11 to 106, the lowest being sands with low water capacity, low humus, low absorptive power for ammonia, low acidity, and those containing a moderate amount of humus.

Acidity of the soil did not prevent the growth of nitrifying organisms, and low water capacity and atmospheric power are not necessarily coincident with low nitrifying power.
N. H. J. M.

Fixation of Atmospheric Nitrogen by Dead Leaves. ED. HENRY (*Bied. Centr.*, 1904, 33, 795—798; from *Ann. Sci. Agron.*, 1903, 8, 313).—Dead leaves of various trees were found to fix considerable amounts of atmospheric nitrogen. No fixation, or very little, was observed when leaves were kept on very dry sand; at the same time, there was no loss of nitrogen.
N. H. J. M.

Changes in the Dimensions and Volume of Vegetable Organs and Tissues under the Influence of Desiccation. MARCELLIN BERTHELOT (*Compt. rend.*, 1904, 139, 825—834).—The results of experiments with stems of *Festuca*, wheat and maize, and leaves of *Gyneryum argenteum* showed that whilst the length was hardly altered by variations in the amount of water present, the diameter changed a good deal. Filter paper, free from ash, did not vary in length and very slightly in width and thickness. Ordinary filter paper varied slightly in width, more in length, whilst the thickness remained constant.
N. H. J. M.

Vegetation in Atmospheres rich in Carbon Dioxide. EM. DEMOUSSY (*Compt. rend.*, 1904, 139, 883—885).—Sixteen different plants were grown in normal air and in air containing 0.15 per cent.

of carbon dioxide. Fifteen of the plants gave much more dry matter in presence of the larger amount of carbon dioxide than in ordinary air, the amounts being as 122 to 262:100. The sixteenth plant, *Fuchsia*, produced 97 of dry matter with carbon dioxide against 100 in normal air, and this may have been due to other conditions of the experiments.

N. H. J. M.

Assimilation of Certain Ternary Substances by Vegetables.

PIERRE MAZÉ and A. PERRIER (*Ann. Inst. Pasteur*, 1904, 18, 721—747).—Sugars, glycerol, and methyl and ethyl alcohols retard for some days the germination of grains of maize, but do not inhibit the growth of the small plants. Sugars are assimilated in the dark, but light is essential for sugar synthesis. These substances added to a mineral solution are actively assimilated in the light, concurrently with those which result in chlorophyllic function. The plants grow more quickly than control specimens. These organic materials therefore contribute to plant anabolism. Glycerol is also absorbed in the light, but it hinders development. Ethyl alcohol is harmful, and leads to the production of aldehyde. Methyl alcohol activates vegetation and is presumably absorbed. The tolerance of plants to alcohols varies a good deal. Dextrin sometimes causes chlorosis; in this condition, produced by want of iron, the result is partly due to excess of bases which fix the iron.

W. D. H.

Decomposition of Fallen Leaves. ED. HENRY (*Bied. Centr.*, 1904, 33, 793—794; from *Ann. Sci. Agron.*, 1902—1903, 8, 328).—Leaves of aspen, when kept over sand in wooden boxes, lost, in eleven months, 52 per cent., and when chalk was employed instead of sand, 45 per cent. The much lower results obtained in earlier experiments are now shown to be due to zinc boxes having been employed. Leaves of *Carpinus betulus*, which are much less leathery and contain less tannin than oak leaves, do not decompose more quickly than the latter.

N. H. J. M.

Formation and Distribution of the Essential Oil of an Annual Plant. EUGÈNE CHARABOT and G. LALOUÉ (*Compt. rend.*, 1904, 139, 928—929).—The essential oil migrates from the leaves to the flower along with carbohydrates. After fructification, the migration of nutritive matters to the flower ceases, and the essential oil seems to return to the leaves.

In the plant examined (basil), it was found that most of the essential oil is in the leaves and flowers. The stems only contain a little, and the roots none at all.

N. H. J. M.

Occurrence of Ricinine in Young Ricinus Plants. ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1904, 43, 211—221).—The compound described as ricidine (Abstr., 1898, i, 42) is now shown to be identical with ricinine, $C_8H_8O_2N_2$ (Maquenne and Philippe, Abstr., 1904, i, 339). It gives a characteristic reaction very similar to the murexide reaction, and also gives the Weidel reaction. The amounts present in young etiolated, or even green, plants are some

12—15-fold that contained in the same number of seeds. So far tyrosine and lycine have not been obtained from these plants.

J. J. S.

A Substance which Inhibits the Fat-splitting Action of the Seed of *Abrus Precatorius*. KARL BRAUN (*Chem. Zeit.*, 1905, 29, 34. Compare Abstr., 1903, ii, 748).—An aqueous extract of the seeds of *Abrus precatorius* was injected subcutaneously into rabbits, the serum from which was then used in the experiments described. The aqueous extract itself was added to castor oil and the slight amount of hydrolysis of the latter estimated. The addition of the serum lessened the extent of this hydrolysis when the latter was conducted at low temperatures.

A. McK.

Presence of Trehalase in Fungi. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1904, 139, 874—876).—Trehalase was found in the tops of *Boletus edulis*, *B. aurantiacus*, and *Cortinarius elatior*, but not in the tubes and lower parts. It also occurs in *Paxillus involutus* and *Russula delica*, and in smaller quantity in *Boletus badius* and *Amanita muscaria*.

N. H. J. M.

Medicinal and Useful Plants of Brazil. THEODOR PECKOLT (*Chem. Centr.*, 1904, ii, 1618—1619; from *Ber. Deut. Pharm. Ges.*, 14, 372—388. Compare Abstr., 1904, ii, 764).—Most of the following Labiatae:—*Ocimum basilicum*, *O. carnosum*, *O. micranthum*, *Aeolanthus suavis*, *Peltodon radicans*, *Heptis spicata*, *Hyptis Salzmanni*, *Heptis fasciculata*, *Cunila galioides*, *Salvia splendens*, *Leonurus sibiricus*, *Leonitis nepetefolia*, and *Scutellaria uliginosa*—contain considerable quantities of ethereal oils and resins, often together with an amorphous bitter principle; glucosides and alkaloids are, however, seldom present in these plants. The abstract contains some account of these substances, which are prepared in most cases from the leaves; the yields and the quantitative composition of various parts of the plants are also given.

E. W. W.

Proteids of Wheat Gluten and its Relations to the Baking Properties of Wheat Flour. JOSEF KÖNIG and P. RINTELEN (*Zeit. Nahr. Genussm.*, 1904, 8, 721—728. Compare Abstr., 1904, i, 1066).—The amounts of water, ash, total nitrogen, nitrogen in substances soluble in 65—70 percent. alcohol, nitrogen as gluten, and the total gluten were determined in seven samples of wheat flour and in three samples of spelt wheat flour. The quality of the flour was also ascertained by making loaves, the actual volume of the loaves being determined by Kreusler's and Maurizio's method. The results showed that one of the spelt loaves was of bad quality, although the meal, as regards gluten proteid soluble in alcohol, did not differ from ordinary wheat-meal. The quality, therefore, depends as little on the gluten alone as on the relation of total gluten, or of the insoluble portion, to the portion soluble in alcohol.

N. H. J. M.

Composition of Rice Refuse. GEORGE S. FRAPS (*Chem. Centr.*, 1904, ii, 1430; from *Bull. Texas Agr. Exper. Stat.*, 73, 3).—The composition of rice hulls is similar to that of wheat straw. The bran, consisting mainly of the seed-skin without much of the hulls, should contain at least 10 per cent. of proteids and not more than 20 per cent. of crude fibre. Addition of hulls lowers the value. The mixture of bran, meal, and hulls, in the proportions present in the whole seed, contains about 7.5 per cent. of proteids and 28 per cent. of crude fibre; its value is about half that of the pure bran. N. H. J. M.

Volatile Fatty Acids in Cheese. Biology of the Cheese Ferment. ORLA JENSEN (*Centr. Bakt. Par.*, 1904, ii, 13, 161—170, 291—306, 428—439, 514—527, 604—615, 687—705, and 753—765).—Acetic and formic acids were always found to be present, the latter, however, frequently only in traces. Cheeses, the ripening of which depends chiefly on mould fungi, contain only small amounts of acetic and formic acids. All other cheeses contain some, and often considerable amounts of, propionic acid.

Valeric acid was only found in Backstein cheese, made by the Limburg method, but traces probably occur in all kinds of cheese.

Rennet cheeses do not contain appreciable amounts of butyric acid, owing, probably, to the low temperature of cheese ripening and the consequent luxuriance of the lactic ferment. Schabzeiger cheese, in which the lactic ferments are killed, contains considerable amounts (0.45 per cent.) of butyric acid.

Cheeses in which a considerable decomposition of fat has taken place generally contain a good deal of ammonia, but in no case was sufficient ammonia found to show an alkaline reaction with phenolphthalein. Alkalinity, as indicated by litmus, often occurs with soft cheeses.

As regards the aromas of different cheeses, amino-acids are prominent in Emmenthaler cheese, butyric esters in Roquefort, and products of putrefaction in Limburger cheese.

Bacillus casei limburgensis alone produces only primary albumoses. *Micrococcus casei liquefaciens*, *Paraplectrum fetidum*, and *B. nobilis* produce chiefly peptones, amino-acids, and ammonia. N. H. J. M.

Lime Requirements of Hessian Soils. TH. DIETRICH (*Bied. Centr.*, 1904, 33, 814—818; from *Ber. landw. Versuchs-Stat. Marburg*, 1903).—Application of lime (as burnt lime, lime marl, and dolomite marl) was beneficial in the case of the lighter soils, from sand to sandy loam. Well cultivated soils which contain little lime can do without liming better than badly cultivated soils, possibly because of the presence of calcium compounds other than carbonate, such as humate and sulphate. Calcium silicate, which occurs in less cultivated soils, is probably unable to take the place of calcium carbonate.

N. H. J. M.

Manurial Value of Human Excrement. JOHN SEBELIEN (*Bied. Centr.*, 1904, 33, 805—808; from *Tidsskr. Norsk. Landbr.*, 1904, 45—55, and *J. Landw.*, 1904).—The results of experiments with oats

showed the value of fæces as a nitrogenous manure to be 75 as compared with sodium nitrate = 100. The value, however, when compared with a mixture of sodium nitrate with phosphatic and potassium manure, was 63 per cent. The nitrogen of urine is shown to be about equal in value to that of sodium nitrate.

Notwithstanding the considerable manurial value of fæces, the conclusion is drawn that, as regards the total excreta, the fæces are only one-ninth the value of the urine, as the latter is produced in so much larger quantity.

N. H. J. M.

Analytical Chemistry.

Sodium Nitrate containing Perchlorate. HENRI PELLET and G. FRIBOURG (*Bied. Centr.*, 1904, **33**, 798—803; from *Ann. Sci. Agron.*, 1902—1903, **8**, ii, 199).—The amounts of perchlorate vary from traces to 1.5 per cent., but as much as 3.2 and even 6 per cent. reckoned as potassium salt have been found. According to de Caluwe, less than 1 per cent. of sodium perchlorate is injurious to vegetation, whilst potassium perchlorate and chlorate are much less injurious.

When sodium nitrate contains perchlorate, the chlorate is present only in small quantity. Potassium is always present, but seems to have no relation to the amount of perchlorate.

Vincente and Lafitte detect chlorates, in presence of chlorides, perchlorates, and nitrates, by adding to the solution a few drops of a solution of aniline in water (1:40) and an equal volume of hydrochloric acid of 22° B. A reddish-violet coloration, which turns to an intense blue, is produced when traces of chlorate are present.

N. H. J. M.

Use of Chromates of Barium and of Silver in the Estimation of Sulphates and Chlorides. LAUNCELOT W. ANDREWS (*Amer. Chem. J.*, 1904, **32**, 476—480).—*Estimation of Sulphates.*—The process published by the author in 1890 consisted in precipitating the alkali sulphate with a solution of barium chromate in dilute hydrochloric acid; after removing the excess of barium chromate by neutralisation, the alkali chromate formed in the reaction was estimated iodometrically. The author now states that in practice it will be found more convenient to use a solution of barium chromate in *N*-trichloroacetic acid, which, unlike the hydrochloric acid solution, is perfectly stable.

Estimation of Chlorides.—Silver chromate is a valuable reagent for the estimation of very small quantities of chlorine, say, in drinking-waters. On agitating the water with this reagent, silver chloride is formed, and the filtrate contains alkali chromate, which may then be estimated colorimetrically.

L. DE K.

Estimation of Tellurium. ALEXANDER GUTBIER (*Chem. Centr.*, 1904, ii, 1554—1555; from *Sitzungsber. phys. med. Soc.*, 1904, 130—133).—The tellurium is separated by reduction with hydrazine hydrate, washed with lukewarm water, and dried, preferably, in a current of hydrogen.

L. DE K.

Iodometric Estimation of Telluric Acid. ALEXANDER GUTBIER and F. RESENSCHECK (*Chem. Centr.*, 1904, ii, 1555; from *Sitzungsber. phys. med. Soc.*, 1904, 138—142).—Telluric acid cannot be accurately estimated by distillation with hydrochloric acid and subsequent iodometric estimation of the chlorine evolved.

L. DE K.

Estimation of Nitrogen in Organic Compounds. HENRY C. SHERMAN and M. J. FALK (*J. Amer. Chem. Soc.*, 1904, 26, 1469—1474).—The authors state that even in the case of alkaloids the Kjeldahl method, as modified by Dyer, may be successfully employed if the boiling be continued for at least two hours after the liquid has become colourless (compare Dyer, *Trans.*, 1895, 67, 812).

L. DE K.

Volumetric Estimation of Hydroxylamine by means of Tervalent Titanium. ARTHUR STÄHLER (*Ber.*, 1904, 37, 4732—4733).—Hydroxylamine is quantitatively reduced to ammonia by titanium trichloride or trisulphate, and, since the excess of the titanium salt can be easily estimated by titration with permanganate or ferric chloride, a convenient method of estimating hydroxylamine, especially in organic compounds, is obtained. Hydrazine sulphate is not acted on by titanium salts under like conditions.

E. F. A.

Estimation of Phosphorus in Iron Ores. JAMES S. ROWLAND and LLEWELLYN J. DAVIES (*J. Soc. Chem. Ind.*, 1904, 23, (24), 1186—1187. Compare *Trans.*, 1866, 19, 148).—One to two grams of the finely powdered ore are mixed with one gram of calcined magnesia and heated in a muffle furnace at a bright red heat for about an hour. The cooled mass is boiled with 50 per cent. nitric acid, when a solution containing all the phosphorus is obtained. The phosphorus is then precipitated by ammonium molybdate and the washed precipitate dissolved in a definite volume of standard sodium hydroxide solution, which is then titrated with nitric acid, using phenolphthalein as indicator. Results are given to show the accuracy of the process.

H. M. D.

Estimation of Phosphoric Acid in Food-stuffs. ÉMILE FLEURENT (*Bull. Soc. chim.*, 1905, [iii], 33, 101—103).—The author finds that Garola's process (*Abstr.*, 1897, ii, 596) for the estimation of phosphoric acid in wheat flour is inconvenient. Larger quantities of material may be used and the operation carried out more rapidly if the flour is destroyed with fuming nitric acid and the product from this operation treated with sulphuric acid, as in the Kjeldahl process, for the final destruction of the organic matter. The residue so obtained is diluted,

neutralised with ammonia, some ammonium chloride added, and the phosphoric acid estimated with "magnesia mixture." T. A. H.

Colorimetric Estimation of Phosphates. OSWALD SCHREINER and BAILEY E. BROWN (*J. Amer. Chem. Soc.*, 1904, **26**, 1463—1468. Compare Abstr., 1904, ii, 85).—The process may be briefly summarised as follows. The solution, drinking water for instance, is mixed with a drop of ammonia and a few drops of ammonium oxalate and evaporated to dryness. The residue is moistened with magnesia mixture, and after a few hours it is washed several times with small quantities of ammonia water and finally once with plain water.

The precipitate, which now contains any phosphoric acid as triple phosphate, is dissolved in nitric acid and tested colorimetrically by the authors' improved molybdate process. L. DE K.

Estimation of Arsenic. R. C. COWLEY and J. P. CATFORD (*Pharm. J.*, 1904, **73**, 897).—The following manner of applying Reinsch's test is described. A fine copper wire, coiled into a helix, is immersed in 10 c.c. of the liquid to be tested, to which 2 c.c. of hydrochloric acid have been added. The liquid is contained in a test-tube and the copper helix should reach from the bottom of the liquid to above its surface. The test-tube and its contents are placed for 1 hour in a salt-water bath kept at a temperature just below its boiling point. At the end of this time, the exposed length of wire is pressed down below the surface and the heating continued for a further 15 minutes. If all the arsenic has been removed from the liquid, this upper portion of the wire will remain bright. The helix is then removed, washed, and the arsenical deposit dissolved off by 1 c.c. of bromine water containing a little hydrobromic acid. After washing the wire, the arsenical solution is treated with 1 c.c. of potassium hydroxide solution and boiled until the light green copper compounds are decomposed. The copper oxides are collected on a filter, the arsenate in the filtrate reduced to arsenite and titrated with *N*/100 iodine solution. The latter should be standardised with an arsenical solution of known strength. It is asserted that the method is capable of measuring 0.033 milligram of arsenic. W. P. S.

Examination of Drugs for Arsenic. WILLIAM A. H. NAYLOR and E. J. CHAPPEL (*Pharm. J.*, 1905, **74**, 33, 34).—The authors have examined most of the drugs of the British Pharmacopœia in order to see whether they complied with the limits proposed in the recently issued report presented to the Pharmacopœia Committee of the General Medical Council. The methods employed were those recommended in this report. A large proportion of the drugs, &c., came within the prescribed limits for arsenic, the exceptions being: antimony oxide, 1000; bismuth carbonate, 5; glycerol, 4; iron, 500; potassium carbonate, 4; reduced iron, 100; sulphonol, 6; and tartarated antimony, 500 parts of arsenic per million. The drugs were purchased through the ordinary channels, the only stipulation made being that they should answer the requirements of the Pharmacopœia. The inference drawn from the results of the experiments is that the

recommendations as to the arsenic limit are, except in the case of a few drugs, capable of practical fulfilment.

W. P. S.

Rapid Estimation of Silicon in Ferrosilicon. LOUIS LUCCHÈSE (*Ann. Chim. anal.*, 1904, **9**, 452—453).—0.5—1 gram of the finely powdered sample is treated in a weighed platinum crucible with 1 c.c. of hydrofluoric acid, 1 c.c. of nitric acid is added, and the whole evaporated to dryness. After adding another c.c. of hydrofluoric acid and evaporating, the mass is calcined. After another treatment with hydrofluoric and nitric acids, the mass is finally ignited to constant weight, and the resulting ferric oxide multiplied by 0.7 represents metallic iron, which, deducted from the original weight, gives the silicon. The impurities present in commercial samples are not sufficiently large to affect the result.

L. DE K.

The Microscopic Examination of Metals. JOHN H. B. JENKINS and D. G. RIDDICK (*Analyst*, 1905, **30**, 2—15).—This paper deals mainly with the microscopic examination of mild steel. The methods of preparing the sections are fully described, and include the polishing, etching, heat-tinting, and mounting of the specimens. Forty-one photo-micrographs are given to illustrate the specimens mentioned in the paper, comprising iron crystals, pig irons, mild steels, cemented steels, manganiferous steels, pearlite, copper, "burnt" copper, annealed steel, flaws in steel, cast-steel, &c.

W. P. S.

Precipitation of Barium Bromide by Hydrobromic Acid. NORMAN C. THORNE (*Amer. J. Sci.*, 1904, [iv], **18**, 441—444).—If a concentrated solution of barium bromide or chloride is treated with an excess of a mixture of equal parts of hydrobromic acid and ether, the barium is precipitated quantitatively as bromide. It is advisable to saturate the mixture with hydrogen bromide, which is conveniently made by dropping liquid bromine into a solution of naphthalene in petroleum and passing the evolved gas through a purifying tower charged with glass wool and red phosphorus. The precipitate is collected on a weighed asbestos pad, washed with the acid ether mixture, mixed with a little ammonium bromide, and finally heated at 250° to constant weight. The process may be used in the presence of calcium and magnesium.

If, however, barium bromide is treated with hydrochloric acid and ether, it is practically precipitated as chloride. If barium chloride is partially precipitated with hydrochloric acid and then mixed with an amount of hydrobromic acid which by itself would not have caused any precipitate, a mixture of barium chloride and bromide is obtained.

L. DE K.

Estimation of Lead and Antimony as Sulphides. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1904, [iii], **31**, 1300—1303).—It is proposed to precipitate the sulphides of these metals in warm, slightly acid solution and to wash the precipitates, previously collected on tared filters, successively with (1) a solution of hydrogen sulphide in water, (2) alcohol (95 per cent.), (3) a mixture of equal volumes of alcohol, ether,

and carbon disulphide, and (4) ether, and then to dry them under reduced pressure over sulphuric acid. The results of a number of trials of this method quoted in the original indicate that it gives trustworthy results.

T. A. H.

Analysis of Lead Minerals. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1904, [iii], 31, 1303—1306).—The finely powdered mineral is warmed with nitric acid for 12 hours, and the residue, left after evaporation of the excess of acid, treated first with warm water and then with hydrochloric acid at 80°. From the aqueous solution, the iron is precipitated by the addition of sodium acetate and subsequent ebullition, and the silver as the chloride. To the filtrate are added (a) the hydrochloric acid solution prepared from the original residue, and (b) the precipitate of basic ferric acetate previously dissolved in hydrochloric acid, and the whole is largely diluted with water, then warmed, and saturated with hydrogen sulphide. The precipitate is first washed with a solution of sodium or ammonium sulphide, arsenic being estimated as magnesium ammonium arsenate, and antimony as the sulphide (compare preceding abstract) in the washings; next the residue is washed with alcohol, &c., as already described (*loc. cit.*), and weighed. If copper is present, this is determined by treating an aliquot portion of the precipitate with nitric acid followed by sulphuric acid, and estimating the copper in the soluble portion by one of the usual methods. The lead sulphide precipitate may also contain a small quantity of silver sulphide; this may be estimated by reduction and cupellation. The remaining constituents of the mineral are determined in the usual way.

T. A. H.

Analysis of Ferrosilicons; Use of Sodium Peroxide in Platinum Crucibles. LOUIS LUCCHÈSE (*Ann. Chim. anal.*, 1904, 9, 450—451).—When copper or nickel crucibles are used for fusions with sodium peroxide, the fused mass is always contaminated with copper or nickel oxides, which complicates the analysis. No such inconvenience is experienced when using a platinum crucible.

For the assay of ferrosilicon, 1 gram (or less) of the finely powdered sample is mixed by means of a spatula with 2 grams of dry sodium carbonate and 2 grams of sodium peroxide contained in a platinum crucible. After heating for 5 minutes very gently over a small Bunsen flame or a spirit lamp, the crucible is seized with a pair of nickel tongues and, with constant rotary movement, heated to dull redness for 15 minutes, when the fused mass is at once turned out. The mass, which contains the silicon as silicate, is then analysed as usual. L. DE K.

Estimation of Chromium in Steel. FRED IBBOTSON and R. HOWDEN (*Chem. News*, 1904, 90, 320—321).—The sample is dissolved in a small amount of nitric acid of sp. gr. 1.20 and heated to expel nitrous fumes. After copious dilution, 2—3 grams of ammonium persulphate and about 0.01 gram of silver nitrate are added and the solution heated until the chromium and manganese are completely oxidised. If the quantity of the latter metal be large, manganese dioxide may separate, and must be removed by filtration. The solution is cooled, treated with excess of ammonium acetate, and lead

acetate solution is added. The precipitated lead chromate is collected on an asbestos filter, washed with dilute ammonium acetate solution, and then dissolved off the filter with nitric acid. After diluting the solution, an excess of standard ferrous sulphate solution is added, and the estimation completed by titration with $N/20$ potassium permanganate solution.

Steels containing large quantities of tungsten cannot be completely decomposed by nitric acid alone. In this case, 0.5 gram of the sample is heated with 10 c.c. of sulphuric acid (1:4) until nearly dissolved, 2 c.c. of nitric acid of sp. gr. 1.2 are then added, and, after boiling, 100 c.c. of water. To this solution, containing much of the tungsten as precipitated oxide, 20 c.c. of the nitric acid and 20 c.c. of a 0.2 per cent. silver nitrate solution are added, together with 3 grams of ammonium persulphate. The mixture is gradually brought to boiling, then cooled, ferrous sulphate solution is added, and the titration completed as above described.

W. P. S.

Estimation of Chromium in Steel. FRED IBBOTSON and R. HOWDEN (*Chem. News*, 1905, **91**, 3).—Chromium and manganese may be estimated in one portion of a sample of steel according to the following method. The manganese is oxidised in a cold nitric acid solution of the steel by means of sodium bismuthate and titrated in the usual manner. About 50 c.c. of nitric acid of sp. gr. 1.2 and 10 grams of sodium bismuthate are then added and the mixture boiled. A small quantity of manganous sulphate is added and the boiling continued for a minute or so. The manganic oxide is then collected on a filter and the chromic acid estimated in the filtrate.

W. P. S.

Electrolytic Estimation and Separation of Antimony and Iron. The Trisulphide Method for Estimating Antimony. ARTHUR FISCHER (*Zeit. anorg. Chem.*, 1904, **42**, 363—417. Compare Abstr., 1903, ii, 616).—The electrolytic reduction of tin from the solution of the tin ammonium thio-salt is easily accomplished by means of a platinum cathode covered by a layer of tin, on the addition of sodium sulphite to the ammonium sulphide used. The use of a platinum iridium anode is recommended.

Antimony may be quantitatively separated from a solution of the thioantimonite or from the thioantimonate in sodium sulphide on the addition of potassium cyanide. The presence of polysulphides in the solution prior to electrolysis is immaterial, since they are easily reduced by the potassium cyanide present. A platinum iridium anode is also preferable in this case to a platinum anode.

The electrochemical equivalent of antimony in thioantimonite is $Sb/3$ and in thioantimonate $Sb/5$. The quinquevalency of antimony favours the reversibility of the reaction, whilst the tervalency does not.

The separation of antimony from tin may be effected from sodium sulphide solution to which potassium cyanide is added. The separation is accomplished both when tervalent and quinquevalent antimony compounds are employed. The solution must be saturated at 30° with sodium sulphide and must contain from 2 to 4 grams of sodium hydr-

oxide. The temperature must not exceed 30° nor the tension 1.1 volts.

In the absence of potassium cyanide, only trivalent antimony can be separated from tin with accuracy. The electrolyte must, in this case, be saturated at 50° with sodium sulphide, and the tension must not exceed 0.9 volt.

Sodium hydrosulphide is unsuitable for the separation, since the potentials of antimony and tin towards its solution are only very slightly different.

The addition of sodium hydroxide to the electrolyte, as recommended by Classen, is absolutely essential.

The trisulphide method for estimating antimony gives results lower than those obtained by the electrolytic method. A. McK.

Estimation of Chloroform Vapour by a Tonometric Method.

B. J. COLLINGWOOD (*Proc. physiol. Soc.*, Nov., 1904, ii—iii; *J. Physiol.*, 32).—The principle of the method is as follows: one chamber contains the mixture of air and chloroform, another air only; the two are connected by a manometer. An equal amount of chloroform is added to both, and the difference in the levels of the water or mercury in the two limbs of the manometer is proportional to the percentage of the chloroform originally present. The method gives good results, and these are not affected by the presence of carbon dioxide.

W. D. H.

Estimation of Chloroform Vapour in Air. ALFRED G. LEVY (*Proc. physiol. Soc.*, Nov., 1904, iii—iv; *J. Physiol.*, 32).—Waller's densimetric method was compared with Vernon Harcourt's combustion method. The results agree very closely, the former method giving as a rule slightly higher results.

W. D. H.

Estimation of Glycerol in its Solutions by means of the Specific Gravity. C. STIEPEL (*Chem. Centr.*, 1904, ii, 1626—1627; from *Seifensiederzeit.*, 31, 818).—The amount of glycerol in a crude sample which is reasonably free from other organic matters may be determined by subtracting from the percentage, as deduced from the sp. gr., the percentage of ash multiplied by 3.33. This, however, only holds good for small amounts of salts. If the sample is very concentrated, the determination of the sp. gr. is somewhat troublesome. In this case, it may be slightly diluted with a known weight of water. L. DE K.

Assay of Glycerol. TAUREL (*Chem. Centr.*, 1904, ii, 1258; from *Mon. Sci.*, 18, 574—577).—When testing crude glycerol by means of Hehner's dichromate process, it is necessary to first remove certain objectionable matters by addition of basic lead acetate. The author prepares this by dissolving 1 mol. of lead acetate and adding half a mol. of sodium hydroxide. Any excess of lead in the filtrate must be carefully removed by sodium sulphate. Alkaline samples should be first neutralised with acetic acid before clarifying with the lead. If there is much sodium chloride present, there is a risk of chlorine escaping during the heating with potassium dichromate and sulphuric acid.

The author therefore recommends connecting the flask with a bulb tube containing a standard solution of arsenious acid, and in this way estimating the chlorine and allowing for it. When testing glycerol for sulphides, acetic acid should be used in the cold. When testing for arsenic by Gutzeit's test, any sulphur compounds should be first fully oxidised with potassium permanganate before adding zinc and hydrochloric acid.

L. DE K.

New Test for Cholesterol. CARL NEUBERG and DORA RAUCH-WERGER (*Chem. Centr.*, 1904, ii, 1434—1435; from *Festschr. für Ernst Salkowski*, 279—285).—A trace of cholesterol is heated with 1.5 c.c. of absolute alcohol, and a minute particle of rhamnose or a drop of solution of δ -methylfurfuraldehyde is added. When quite cold, an equal bulk of sulphuric acid is allowed to run down the sides of the test-tube, when a characteristic raspberry-red ring will at once be noticed. If the tube is well cooled and shaken, the whole liquid becomes red and shows, after being diluted with alcohol, a characteristic dark absorption band between *E* and *C*. If the mixture becomes overheated, the liquid assumes a brown colour, and then shows a second absorption band in the neighbourhood of *D*. Phytosterol does not give the reaction, or at most a rose colour which gives an absorption band in the yellowish-green.

The reaction is, however, shared by some hydroaromatic compounds, such as biliary acids, also by camphor, borneol, menthol, and similar substances.

L. DE K.

Corrections to be Applied in the Estimation of Lactose in Cows' Milk and Human Milk. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1904, [vi], 20, 501—505).—Attention is drawn to the necessity of correcting for the volume of the precipitated casein and fat in this estimation, particularly when the analysis is made on the undiluted milk. Lactose cannot be estimated polarimetrically in human milk on account of the presence of a laevorotatory substance which is not precipitated by mercuric nitrate or by picric acid. As this substance, however, does not reduce Fehling's solution, the volumetric method may be used.

W. P. S.

New Reaction for Lactose (and Maltose). ALFRED WÖHLK (*Zeit. anal. Chem.*, 1904, 43, 670—679).—Lactose or maltose heated with 10 per cent. ammonia for 15—20 minutes develops a bright madder-red colour, of considerable permanence. Other carbohydrates give either no colour or a yellow to yellowish-brown one, and do not obscure the lactose reaction. The reaction is, however, inhibited by various substances, such as tartrates, citrates, and ammonium salts.

M. J. S.

Composition and Analysis of Maple Syrup and Maple Sugar. JULIUS HORTVET (*J. Amer. Chem. Soc.*, 1904, 26, 1523—1545).—A lengthy paper giving the results of the analysis of a large number of pure and adulterated samples of maple sugar and syrup. For full particulars of the analytical operations and results, the original paper

should be consulted. Considerable importance is attached to the volume occupied by the precipitate formed on adding basic lead acetate. The amount of malic acid and the alkalinity of the ash also give valuable indications as to the genuineness of the samples.

L. DE K.

Table for the Rapid Calculation of the Original Extractive Matter of Beer Wort. PAUL LEHMANN and HERMANN STADLINGER (*Zeit. anal. Chem.*, 1904, **43**, 679—687).—The formula,

$$\epsilon = \frac{100(E + 2.0665A)}{100 + 1.0665A}, \text{ for}$$

the calculation of the original extractive matter, ϵ , from the percentage of alcohol, A , and the extractive matter of the beer, E , may be expressed in the form

$$\epsilon = E \frac{100}{100 + 1.0665A} + \frac{206.65A}{100 + 1.0665A}, \text{ or}$$

$\epsilon = E.(A\alpha) + (A\beta)$. The table gives the values for $A\alpha$ and $A\beta$ for each 1/100 per cent. of alcohol from 1.5 to 4.99 per cent., and the calculation is thereby resolved into the multiplication of the factor $A\alpha$ by E , and addition of the corresponding number $A\beta$. M. J. S.

Estimation of Carbamates. JOHN J. R. MACLEOD and H. D. HASKINS (*Amer. J. Physiol.*, 1904, **12**, 444—456).—Carbamates are present in the urine when urea formation is interfered with. Previous methods for detecting these salts are unsuitable for quantitative work. The present paper is limited to a description of a new method and proofs of its accuracy. The principle of the method is to determine the yield of carbon dioxide from the liquid by the Barcroft-Haldane method, and again in the same liquid after precipitation of the carbonates by barium hydroxide and ammonia. In liquids which contain proteid, a slight modification is necessary. W. D. H.

Detection of Acetates, Cyanides, and Lithium. STANLEY R. BENEDICT (*Amer. Chem. J.*, 1904, **32**, 480—483).—*Detection of Acetates.*—The process is based on the fact that a solution of cobalt nitrate containing a little free acetic acid gives practically no precipitate with hydrogen sulphide, but does so at once when an alkali acetate is added; also on the fact that silver acetate is slightly soluble.

The solution is mixed with slight excess of sodium carbonate, and then with slight excess of silver nitrate. After carefully removing this by sodium chloride, the filtrate is saturated with hydrogen sulphide. On pouring the liquid into 2 c.c. of *N*-cobalt nitrate containing a few drops of acetic acid and saturated with hydrogen sulphide, a more or less heavy precipitate of cobalt sulphide will be formed should an acetate be present.

Detection of Cyanides in the presence of Ferrocyanides.—The solution is made alkaline with sodium hydroxide, and about 1 c.c. of *N*/25 mercurous nitrate is gently poured over it. A ring of black mercurous oxide is thus formed, which, however, in the presence of a trace of cyanide will on shaking partly dissolve, whilst the rest turns a light grey.

Detection of Lithium in the presence of Sodium.—To the solution is added a little ammonia, and then one-tenth of the volume of *N*/5 sodium phosphate, and finally enough alcohol to produce a fairly heavy permanent precipitate, which may be simply sodium phosphate or contain admixed lithium phosphate. The solution is now heated to boiling, when, should lithium be absent, it will become perfectly clear, but in the presence of lithium its phosphate remains undissolved.

L. DE K.

Detection and Estimation of Citric Acid in Wines. LUCIEN ROBIN (*Ann. Chim. anal.*, 1904, 9, 453—456).—The following reagents are required: (1) a 40 per cent. solution of lead acetate, (2) a mixture of 1 vol. of glacial acetic acid and 9 vols. of water, (3) a strong solution of potassium hydroxide, (4) a mixture of 1 vol. of glacial acetic acid and 9 vols. of alcohol, (5) a hot saturated alcoholic solution of cadmium acetate.

Twenty-five c.c. of wine are heated to boiling, 3 c.c. of (1) are added, and, after boiling for a few minutes, the precipitate is collected, washed, and then heated for 5 minutes at 90° with 10 c.c. of (2). After washing the residue with the acid water, the filtrate is freed from lead by means of hydrogen sulphide and evaporated to incipient dryness. The residue is now dissolved in 5 c.c. of alcohol, and, after being neutralised with (3), 0.5 c.c. of glacial acetic acid is added, and, after stirring, the liquid is passed through a filter and the deposit washed twice with 5 c.c. of (4). After the last traces of potassium hydrogen tartrate have separated and been removed by filtration, the citric acid is precipitated by adding 6 drops of (5), collected on a tared filter, washed with alcohol, dried at 100°, and weighed. The weight multiplied by 0.5378 = citric acid.

After weighing, it may be further identified as a citrate by Denigès' mercurial reagent.

L. DE K.

Estimation of Amino-acids in Urine. FRANZ ERBEN (*Zeit. physiol. Chem.*, 1904, 43, 320—324).—An adaptation of the method already employed by E. Fischer and Bergell, and by Ignatowski, in which naphthalene- β -sulphonic chloride is the reagent employed. Normal urine contains a conjugated amino-acid, hippuric acid, which does not give the reaction in question. In the investigation of urine, it is first necessary to remove and estimate the hippuric acid. When this is done, normal urine and many pathological urines give no further evidence of amino-acids. From experiments with mixtures of urine and amino-acids (glycine, alanine, leucine, tyrosine), the method is shown not to be accurate quantitatively, from 57 to 80 per cent. only of the added acid being recoverable.

W. D. H.

The Reactions Concerned in the Estimation of the Iodine Value. FREDERIK H. VAN LEENT (*Zeit. anal. Chem.*, 1904, 43, 661—670).—From a discussion of the work of von Hübl, Waller, Ephraim, Marshall, Wijs, and others, the author draws the following conclusions: (1) the active constituents of the solutions of von Hübl, Ephraim, and Wijs are iodine monochloride and hypiodous acid;

both of these form additive products and are iodometrically equivalent, (2) no combination or liberation of hydrochloric acid takes place during the iodine absorption, (3) the hydrochloric acid which becomes free during the reaction is a product of the hydrolytic decomposition of iodine monochloride, (4) no substitution of hydrogen by halogens takes place, (5) the iodine value is a measure of the unsaturated compounds present in the fat, (6) the Wijs solution of iodine monochloride in 99 per cent. acetic acid is to be preferred for the reaction.

M. J. S.

A Simple Method for the Estimation of the Fat in Butter.

A. HESSE (*Zeit. Nahr. Genussm.*, 1904, 8, 673—675).—From 1.5 to 2 grams of the well-mixed sample are placed in a Gottlieb's cylinder and treated with 8 c.c. of hot water. If necessary, the cylinder is placed in warm water until the butter is melted. One c.c. of ammonia and 10 c.c. of alcohol are then added, and the mixture shaken to dissolve the casein. After cooling, 25 c.c. of ether and 25 c.c. of light petroleum are added, and the whole thoroughly mixed. When the ethereal solution of the fat has separated, it is drawn off and the residue again treated with 50 c.c. of ether, which is drawn off without having been shaken up, and finally with 50 c.c. of the mixture of ether and petroleum. The united ethereal solutions are evaporated and the residue of fat weighed.

W. P. S.

The "Sinacid" Butyrometer. DU ROI and KOEHLER (*Milch. Zeit.*, 1904, 33, 787—790).—This instrument, devised by A. Sichler, is intended for the estimation of fat in milk, the method of procedure resembling that of Gerber. Its name is derived from the fact that the sulphuric acid of the latter process is dispensed with (*sine acido*), a salt solution being used instead. The composition of this solution is not given, as the patent rights have not yet been secured, but it has an alkaline reaction. The amyl alcohol of the Gerber process is replaced by another higher alcohol. The new method gives results closely agreeing with those yielded by Gerber's process, but the authors consider that the latter is to be preferred where many samples of milk have to be examined, on account of its rapidity.

W. P. S.

Colour Reaction of Cotton Seed Oil. GEORGES HALPHEN (*Bull. Soc. chim.*, 1905, [iii], 33, 108—110).—It is shown that, after cotton seed oil has been fully brominated, it does not give Halphen's colour reaction (Abstr., 1898, ii, 358), but that oil coloured by the reagent retains its colour on subsequent bromination. The substance to which the production of the colour is due is not present in the "unsaponifiable matter," and is probably an unsaturated acid. When cotton seed oil is treated with water, the "active principle" is not removed, but wet oil gives an orange-brown colour instead of the normal red colour with Halphen's reagent. The passage of hydrogen sulphide through cotton seed oil produces no coloration. These observations do not support Raikow's view (Abstr., 1900, ii, 698, and 1902, ii, 366) that the production of the red colour is due to the formation of

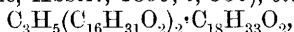
a thio-derivative, and its disappearance on exposure to sunlight to the loss of sulphur and polymerisation of the product formed.

T. A. H.

Detection of Cotton-seed Oil in Olive Oil. E. MILLIAU (*Compt. rend.*, 1904, 139, 807—809. Compare Abstr., 1904, ii, 456).—The chemical tests applied in the detection of cotton-seed oil, namely, the reduction of warm alcoholic silver nitrate solution and the production of a red colour on treatment with a solution of sulphur in carbon disulphide, are both given by "capoc" oil and baobab oil. These oils are, indeed, more sensitive towards both reagents than cotton-seed oil, and a method of distinguishing the two former from cotton-seed oil is based on the observation that the fatty acids from "capoc" oil and baobab oil give an intense brown coloration with alcoholic silver nitrate in the cold, whilst cotton-seed oil in similar circumstances has no reducing action. The oils themselves, if chloroform is added to bring them into solution, may be used instead of the free acids, but the difference of behaviour is less marked.

H. M. D.

Fat of the Fruits of the Dipterocarpus Species. ISIDOR KLIMONT (*Monatsh.*, 1904, 25, 929—932).—A specimen of Borneo tallow, from the Austrian *Handelsmuseum*, melts at 34·5—34·7° and has an acid number 15·8, an iodine number 30·1, and a hydrolysis number 194·6. It contains tristearin, tripalmitin (?), oleodistearin (Henriques and Künne, Abstr., 1899, i, 330), *oleodipalmitin*,



which melts, when freshly recrystallised, at 33—34°, when fused and resolidified at 28—29°, has an iodine number 30·2, a hydrolysis number 202·7, and other mixed glycerides of fatty acids with smaller carbon nuclei, and with unsaturated fatty acids.

Oleodipalmitin is found also in cacao fat (compare Fritzweiler, Abstr., 1902, ii, 470).

G. Y.

Assay of Beeswax. GEORG BUCHNER (*Chem. Zeit.*, 1905, 29, 32—33).—A slight modification of the author's process (Abstr., 1892, ii, 665). After determining the acidity number of 3·6 grams of the sample, 35 c.c. of *N*/2 alcoholic potassium hydroxide are added, and, after connecting the Erlenmeyer flask with a Soxhlet tube and condenser, the contents are boiled briskly for one hour. In this way the liquid in the flask gets temporarily concentrated and the saponification is more complete; a portion of the alcohol also can be recovered from the Soxhlet tube. When very refractory samples have to be tested, the author uses absolute alcohol or pure amyl alcohol (Werder's process).

L. DE K.

Saponification Number and Dry Residue of Oil of Lemon. ENRICO BERTÉ (*Chem. Centr.*, 1904, ii, 1670; from *Boll. Chim. Farm.*, 43, 709—713).—Adulteration of oil of lemon may be detected by means of the saponification number and by the amount of residue left on evaporation on the water-bath. The saponification number of the pure oil does not exceed 3·5, and the residue varies

from 2—3·5; it is therefore possible to detect the presence of excessive quantities of fatty or resinous matters.

A table is also given showing the constants of a pure oil; of a mixture containing 25 per cent. of terpene and 2 per cent. of fatty oil, and another mixture containing 50 per cent. of terpene and 4 per cent. of oil. The data include the rotation at 20°, the rotation of the distillate at 20°, the rotation of the residue at 20°, sp. gr. at 15°, dry residue, and the citral.

L. DE K.

Detection of Saccharin. E. VON MAHLER (*Chem. Zeit.*, 1905, 29, 32).—The ethereal solution containing the saccharin is evaporated to dryness and the residue is transferred to a small reduction tube, in which a small piece of metallic sodium or potassium has been placed. The whole is heated, and, after the action is over the tube while still hot is immersed in a freshly-prepared solution of sodium nitroprusside. If saccharin was originally present, the mass now contains alkali sulphide, which gives the characteristic violet colour.

L. DE K.

The Pyrrole Reaction. CARL NEUBERG (*Chem. Centr.*, 1904, ii, 1435—1437; from *Festschr. für Ernst Salkowski*, 271—278).—A table containing the names of 47 organic compounds which give the pyrrole reaction either directly or after addition of zinc dust or zinc dust and ammonia.

L. DE K.

Reactions of Cocaine and Morphine. C. REICHARD (*Chem. Centr.*, 1904, ii, 1257; from *Pharm. Zeit.*, 49, 855. Compare Abstr., 1904, ii, 374).—A 1 per cent. solution of uranium nitrate containing a few drops of potassium thiocyanate gives an intensely yellow precipitate with salts of cocaine. If a little of a mixture of 5·04 parts of uranium nitrate and 6·58 parts of potassium ferricyanide is dissolved in a few drops of water and added to a few crystals of a cocaine salt, the latter assume a dark colour and gradually yield a dark brown liquid. Morphine crystals at once turn brownish-black and yield a dark red liquid which, on drying, gives an almost black residue. A mixture of 2·5 parts of crystallised copper sulphate and 6·6 parts of potassium ferricyanide rubbed with a few drops of water and a little solid or dissolved morphine at once turns dark brown. Cocaine gives no reaction. A mixture of powdered copper sulphate and morphine when heated with sulphuric acid yields a beautiful dark violet liquid.

L. DE K.

Composition of Turmeric. ALBERT E. LEACH (*J. Amer. Chem. Soc.*, 1904, 26, 1210—1211).—The author has analysed three varieties of turmeric, China, Pubna, and Alleppi. The average composition is as follows:

Moisture, 8·73; total ash, 7·07; ash soluble in water, 5·36; total nitrogen, 1·42, equal to 8·88 proteids; total ethereal extract, 11·17; volatile ethereal extract, 3·19; alcoholic extract, 6·96; crude fibre, 5·37; reducing matters by acid method calculated as starch, 49·73; starch by diastase method, 34·21 per cent.

L. DE K.

New Reagent for the Detection of the Colouring Matters of Blood or their Products of Decomposition. E. RIEGLER (*Zeit. anal. Chem.*, 1904, **43**, 539—544).—The two absorption bands in the spectrum of an alkaline solution of Hoppe-Seyler's hæmochromogen are exhibited with great intensity by an alcoholic solution, and such a solution is very readily obtained by treating blood pigments with an alkaline alcoholic solution of hydrazine. Sodium hydroxide, 10 grams, and hydrazine sulphate, 5 grams, are dissolved in 100 c.c. of water and the solution is mixed with 100 c.c. of strong alcohol and filtered. By shaking a little blood or hæmoglobin with this reagent, a rich purple solution of hæmochromogen is obtained. When shaken with air, this solution becomes transiently green, and in this condition shows the single band of an alkaline hæmatin solution. In testing urine for blood, a trace of white of egg is added and coagulated by boiling after adding a drop of acetic acid. The albumin carries down the hæmatin, and after collection on a filter and washing, is shaken with the hydrazine reagent. Blood stains on linen can be treated directly with the reagent and examined with a micro-spectroscope. M. J. S.

Simulation of Traces of Albumin by Substances which interfere with the Ferrocyanide Test, especially in Liquids requiring Clarification. BRUNO BARDACH (*Zeit. anal. Chem.*, 1904, **43**, 554—557).—In cases where proteids have been precipitated by ammonium sulphate, it is customary to confirm the completeness of the precipitation by testing the filtrate with potassium ferrocyanide. In these circumstances, a trifling turbidity is always observed, and this the author has traced to impurities in the ammonium sulphate, which cannot be removed by any of the ordinary methods of purification. It is necessary, therefore, to employ the purest ammonium sulphate obtainable, and to test the specimen with ferrocyanide and make allowance for the turbidity which is obtained in the absence of albumin. A similar deceptive turbidity is produced by ferrocyanide in liquids which have been clarified by infusorial earth, in consequence of traces of iron from the kieselguhr passing into solution. Neither ignition nor treatment with hydrochloric acid improves the kieselguhr in this respect. The only satisfactory method of clarification is to pass the liquid through several thicknesses of filter-paper, which, however, must be absolutely free from iron. M. J. S.

General and Physical Chemistry.

Refractive Indices of the Elements. CLIVE CUTHBERTSON (*Proc. Roy. Soc.*, 1904, **74**, 283—284).—Attention has been previously drawn to the fact that the refractivities of (1) helium, neon, argon, krypton, and xenon, (2) chlorine, bromine, and iodine are in the ratio of small integers. With a Jamin's refractometer, adapted for high temperatures, the refractivities of mercury, phosphorus, and sulphur have been determined, and it is shown that the simple relationship found in the cases of the inert atmospheric gases and of the halogens holds also in the case of (1) nitrogen and phosphorus, (2) oxygen and sulphur; an atom of the second element in each case retards light four times as much as an atom of the first. On these lines, one may regard the two series N, O, F, Ne and P, S, Cl, A as in some sense homologous. In the latter series, the power to retard light increases with the valency, in spite of the simultaneous decrease in atomic weight. The same relationship is found for the series Ne, O, N. J. C. P.

Spectra of the Metals in the Electric Arc. VII. Spectrum of Tungsten. BERNHARD HASSELBERG (*K. Svenska Vet. Akad. Handl.*, 1904, **38**, No. 5, 1—47. Compare Abstr., 1903, ii, 706).—Although on the whole the same lines occur in the arc spectrum of tungsten as appear in the spark spectrum recently recorded by Exner and Haschek, there is very marked difference in the relative intensity of the lines. The lines in the arc spectrum, which are apparently due to iron, chromium, titanium, cobalt, nickel, manganese, vanadium, and molybdenum, have been eliminated, and the lines regarded by the author as characteristic of tungsten are fully recorded, the discussion being illustrated by reproductions of the spectra. A number of lines in the tungsten spectrum coincide with feeble lines in the solar spectrum, and the author regards it as proved that tungsten is present in the absorbing envelope of the sun. J. C. P.

The Group IV. Lines of Silicon. Sir J. NORMAN LOCKYER and F. E. BAXANDALL (*Proc. Roy. Soc.*, 1904, **74**, 296—298).—In previous papers (Abstr., 1900, ii, 181; *Proc. Roy. Soc.*, **67**, 403), it was shown that the silicon lines might be divided into four distinctive groups. The genuineness of the lines of the fourth group has been questioned by de Gramont (Abstr., 1904, ii, 641), but the authors adhere to the conclusion previously reached, and the photographic evidence on which it was based is now reproduced. J. C. P.

Infra-red Absorption Spectrum of Carbon Dioxide as affected by Pressure. CLEMENS SCHAEFER (*Ann. Physik.*, 1905, [iv], **16**, 93—105).—Under high pressure, the bands are widened and the maximum absorption is intensified. This result cannot be attained merely by increasing the thickness of the absorbing layer,

hence the character of the absorption depends not on the number of absorbing molecules, but on their density. J. C. P.

Rotation of Optically Active Substances. PAUL WALDEN (*Ber.*, 1905, 38, 345—409).—A lecture delivered before the German Chemical Society. C. H. D.

Dissociation of Strychnine Salts determined by their Rotatory Power. Rotatory Power in Homologous Series. Influence of the Double Linking. JULES MINGUIN (*Compt. rend.*, 1905, 140, 243—245).—The author has measured the rotation of a number of strychnine salts, obtained by dissolving 0.334 gram of strychnine and a molecular proportion of the acid in 25 c.c. of a mixture of parts of benzyl alcohol and ethyl alcohol (2:1), and the change in the rotatory power caused by the addition of excess of acid has also been studied. The results show (1) that the salts are partially hydrolysed by the addition of excess of acid, and the hydrolysis, as measured by the increase in the rotatory power, is greater in the case of the weak than of the strong acids; (2) that the salts of a homologous series of acids have practically the same rotatory power (compare Tschugaeff, *Abstr.*, 1898, i, 274, 495; 1899, ii, 3; and Minguin and de Bollement, *Abstr.*, 1903, i, 352); (3) that the salts of the unsaturated acids have a higher rotatory power than those of the saturated acids containing the same number of carbon atoms (compare Haller, *Abstr.*, 1903, i, 503, 563, 628; Zelinsky, *Abstr.*, 1902, i, 597; Rupe, *Abstr.*, 1903, i, 565; Minguin, 1903, i, 428).

M. A. W.

Specific Rotatory Power of Nicotine dissolved in Mixtures of Water and Ethyl Alcohol. T. GNESOTTO and G. CRESTANI (*Nuovo Cim.*, 1904, [v], 8, 365—381).—The authors have measured the specific rotation of nicotine in various mixtures of water and ethyl alcohol, all the solutions having approximately the same concentration, namely, 12.1 grams of nicotine per 100 c.c. of the solution. The results, which are given in the form both of tables and of curves, show that the values of the specific rotatory power of nicotine at 20° in aqueous alcohol are all inferior to those of the specific rotatory power of the substance itself, supposing that each component of the mixture exercises on the active substance an influence proportional to the quantity by weight in which it occurs in the mixture. The differences, Δ , between the absolute values of the specific rotatory power of nicotine determined experimentally and the absolute values calculated on the above supposition, starting from an alcoholic solution of nicotine, increase rapidly with the amount of water substituted for alcohol, and reach a maximum for a mixture of water and alcohol containing about 80 per cent. of the latter; from this maximum point, the differences vary practically rectilinearly with the proportion of water present. From these and previous results, it is concluded that the action of mixtures of water and alcohol on alkaloids shows itself by producing an increase or a diminution in the specific rotatory power of the active substance in solution (with reference to that obtained by

calculation from the additive formula), according as dilution of the solution of the substance in the two separate solvents produces an increase or a diminution in the specific rotatory power. T. H. P.

Fluorescence of Sodium Vapour. L. PUCCIANTI (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 433—440).—The author shows that the lines D_1 and D_2 exist in the fluorescence spectrum of sodium vapour. The exciting light from which they originate is that of these usually broad lines themselves, but in the small spectral interval occupied by each of them light of a given wave-length can excite the emission of waves of different lengths. Indications are given of the construction of a model of the phenomenon on the basis of secondary waves, taking into account the annulment or collision of the vibrations.

T. H. P.

Solvent and Fluorescence. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Zeit. physikal. Chem.*, 1904, 50, 350—354. Compare Abstr., 1904, ii, 528).—An example of the way in which fluorescent amines exhibit a different fluorescence colour according to the solvent in which they are dissolved has already been given (*loc. cit.*). The same phenomenon is exhibited in an exceptional degree by dimethylnaphtheturhodine, also by *o*-aminocinnamic acid and its esters, dimethylaminodiphenylquinoxaline, aminobenzoxazole, and ethyl succinylsuccinate (compare also Kehrmann and Messinger, Abstr., 1892, 889).

It appears that dissociating solvents affect very slightly the fluorescence colour of the solid substance, but the cause of the change of fluorescence cannot be association in benzene and similar solvents, because dimethylaminodiphenylquinoxaline, for example, has a normal molecular weight in benzene. It is shown, however, that in general the displacement of the fluorescence colour from that exhibited by the solid increases as the dielectric constant of the solvent decreases. The order of the solvents is, however, not always the same, so that the nature of the fluorescent substance is also a determining factor.

It is noted that the colour of the solutions of these fluorescent substances changes with the solvent in a manner very similar to the fluorescence colour.

J. C. P.

Action of Very Low Temperatures on the Phosphorescence of Certain Sulphides. P. LE ROUX (*Compt. rend.*, 1905, 140, 84—85, 239—241).—The diminution in the brightness of the phosphorescence of certain sulphides at low temperatures has been observed by Becquerel (Abstr., 1891, 776), Pictet (*Compt. rend.*, 1894, 119, 527), Dewar (*Chem. News*, 1894), Henry (*Compt. rend.*, 1896, 122, 662), and A. and L. Lumière (*ibid.*, 1899, 125, 549), and the author finds that at the temperature of liquid air phosphorescent calcium sulphide becomes non-luminous, but recovers its original luminosity when removed from the liquid air and allowed to regain the ordinary temperature. At the low temperature, the phosphorescence is in a potential state, for the light emitted by the cooled sulphide on regaining the ordinary temperature is more intense than that of a similar specimen which has not been cooled; further, if a

non-luminous specimen of calcium sulphide is placed in liquid air and exposed to the light of burning magnesium, it becomes luminous when heated to the ordinary temperature. M. A. W.

Triboluminescence. II. L. A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1245—1253. Compare Abstr., 1901, ii, 489).—The author has examined a number of crystalline compounds and finds that, in addition to the six compounds already given (*loc. cit.*), benzoyl- β -naphthylamine and benzoyl-*m*-toluidine also exhibit triboluminescence of the first order. With the former of these two compounds, this property can be observed in ordinary daylight, and, under favourable conditions, the emission of light continues for some six or eight seconds.

The results obtained with a number of amino-compounds show that in many cases of two closely-related compounds, such as homologues or isomerides, one exhibits triboluminescence whilst the other does not. Similar observations have been made on other classes of compounds.

Triphenylmethane is triboluminescent, but its compounds with benzene or thiophen of crystallisation do not exhibit this property; on heating these compounds for a short time above their melting points and recrystallising the residues from ether or toluene, triboluminescent crystals are again obtained.

Aniline hydrochloride exhibits strong triboluminescence, but the basic salt, $2\text{NH}_2\text{Ph}\cdot\text{HCl}$, does not do so. Uranium nitrate completely loses its power of triboluminescence if the crystals are recrystallised from ethereal solution over phosphoric oxide.

A number of optically active compounds were examined, and it was found that these exhibit triboluminescence, whilst the corresponding racemic compounds do not. T. H. P.

Radioactivity of Underground Air. H. M. DADOURIAN (*Amer. J. Sci.*, 1905, [iv], **19**, 16—22).—Bumstead has recently shown (*Amer. J. Sci.*, 1904, **18**, 1) that the excited activity obtained by exposing a negatively charged wire in the open air may be fairly accounted for by assuming the presence of radium and thorium emanations in the air. The author now finds that the slowly decaying activity obtained by exposing a negatively charged wire to underground air (that is, air which has passed through the soil) is attributable to thorium.

J. C. P.

Occurrence of Radium and of Radioactive Noble Earths in Fango Mud and Soil from Capri. FRIEDRICH GIESEL (*Ber.*, 1905, **38**, 132—133).—The small amount of crude barium sulphate obtained from Fango mud contains radium. As Capri soil contains no sulphuric acid, it was fractionally extracted with hydrochloric acid; radium was found to be present chiefly in the fraction obtained by extraction of the earth with a large excess of hydrochloric acid. No uranium was found in either earth. G. Y.

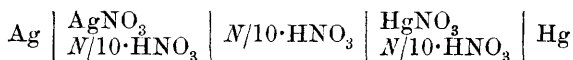
A New Radium Mineral. J. DANNE (*Compt. rend.*, 1905, 140, 241—243).—The pyromorphite in lead ores found at Issy-l'Évêque contains radium in variable quantity, some specimens having a radioactivity several times as great as that of uranium, and 1000 kilos. of the mineral yield one centigram of radium bromide. As the mineral contains no uranium (compare Boltwood, *Abstr.*, 1904, ii, 666), the radium has probably been recently deposited by waters charged with radium salts, for from the waters of springs in the neighbourhood a radioactive gas containing radium emanation has been extracted, and the barium sulphate precipitated by sulphuric acid from a solution of barium chloride in the radioactive water has a permanent, although feeble, radioactivity.
M. A. W.

Potential of the Hydrogen-oxygen Cell. FRANCIS JOSEPH BRISLEE (*Trans. Faraday Soc.*, 1905, 1, 65—74. Compare Wilshire, 1901, ii, 2; Luther and Inglis, 1903, ii, 406).—The influence of small quantities of hydrogen peroxide, persulphuric acid, and ozone on the oxygen potential has been investigated. Two different methods of operation were employed. In the first, the electrodes were polarised by electrolysis extending over two to three days, in the second they were freed from gases as completely as possible to begin with, and the respective gases were then passed through the solution (normal acid or alkali), the potential, as in the first method, being measured at intervals until a constant value was reached. This condition having been attained, the effect of the addition of the various substances was tried.

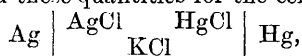
The oxygen potential is lowered by the addition of small quantities of hydrogen peroxide. The presence of persulphuric acid or ozone raises the oxygen potential. In one experiment, in which the concentration of the added persulphate was 1 gram-molecule in 5000 litres, the *E.M.F.* rose from 1.081 to 1.122 volts, and remained constant at this value for five days. Persulphuric acid and ozone appear further to hinder the separation of oxygen from the supersaturated electrodes, and this perhaps accounts for the high potential observed and maintained for a comparatively long period in electrolytically polarised electrodes. A very thin platinum electrode was prepared by coating a glass tube with "Glanz Platin," heating in a muffle furnace, and platinising in the usual way. When this was polarised for 72 hours in normal sodium hydroxide solution, the original *E.M.F.* of the cell was 1.366, but on passing a current of oxygen gas through the solution this rapidly fell to 1.073 (the normal value). Under the same conditions, but with the addition of potassium persulphate (1 gram-molecule in 500 litres), after polarisation, the original *E.M.F.* of 1.350 volts only sank to 1.328 volts at the end of ten days.

The *E.M.F.* of cells provided with very thin platinised electrodes prepared in the manner described is in very good agreement with that calculated from the Helmholtz formula.
H. M. D.

Reduction of Mercurous Chloride by Silver. J. N. BRÖNSTED (*Zeit. physikal. Chem.*, 1904, 50, 481—486).—As shown by Ogg (*Abstr.*, 1899, ii, 14), the potential difference of the cell



alters its sign with the concentration of the silver and mercurous salts, and in the most dilute solutions studied by him the current passed in the cell from silver to mercury. This must therefore be the case also with the cell $\text{Ag} \left| \frac{\text{AgCl}}{\text{KCl}} \right| \frac{\text{HgCl}}{\text{KCl}} \left| \text{Hg} \right.$, and the change going on in this cell may be represented by the equation $\text{Ag} + \text{HgCl} = \text{Hg} + \text{AgCl}$. This, however, is an endothermic reaction, for, according to the work of Thomsen and of Nernst, the heat of formation of mercurous chloride is greater than that of silver chloride. With the help of Helmholtz's equation, $T(d\pi/dT) = \pi - U$, the heat effect of the reaction may be calculated from the *E.M.F.* and the temperature-coefficient of the *E.M.F.* of the corresponding cell. The author has determined these quantities for the cell



and is able to calculate the heat absorbed by the reaction $\text{Ag} + \text{HgCl} = \text{Hg} + \text{AgCl}$ in good agreement with the calorimetric data.

J. C. P.

The Measurement of the Potential of the Electrodes in Stationary Liquids. The Determination of Changes of Concentration at the Cathode during Electrolysis. HENRY J. SAND (*Trans. Faraday Soc.*, 1905, 1, 1—23. Compare Abstr., 1901, ii, 82).—In the cells used for the measurement of the electrode potentials, arrangements were made to have the electrode not under examination as non-polarisable as possible, to avoid the evolution of gases and to permit of the continuous measurement of the difference of potential between the electrode and the layer of solution in contact with it during the passage of the current. The variation of the electrode potential with the time of passage of the current is shown in a series of curves.

With solutions of silver nitrate, copper sulphate, and zinc sulphate, the removal of the dissolved substance from the immediate neighbourhood of the cathode is indicated by a sudden drop in the electrode potential. In the case of copper sulphate, the fall amounts to one volt, and the potential then becomes fairly constant at this lower value. In the case of silver nitrate, the fall is only about 0.2 volt, and afterwards the potential rises more or less rapidly to its original value, the cathode being then found to have become covered with minute silver crystals which grow out into the solution. Zinc sulphate behaves in similar manner to copper sulphate. Diffusion coefficients for the first two salts are calculated on the assumption that the breaks in the curves may be taken as measuring the time which elapses before the concentration of the liquid bathing the electrode becomes zero, and the numbers obtained agree satisfactorily with the known data.

Curves obtained for alcoholic cuprous chloride solutions show two breaks, one corresponding with the reduction of the small quantities of contained cupric salt, the other to the deposition of copper from the cuprous chloride; the latter process begins at 0.45 volt, the electrode

potential rising, however, gradually to 0.65—0.70 volt, at which it remains fairly constant.

The curves for the electrode potential when nitrobenzene is undergoing reduction in acid and alkaline solutions are also given. In acid solution and with a platinum cathode, the potential rises at first, then falls, and again rises, becoming finally stationary. The retrogression appears to be due to temporary alteration in the nature of the electrode as a consequence of the electrolysis. With a copper cathode, similar phenomena are observable, but whilst the original electrode potential has a lower value (corresponding with less absorption of energy), the final stationary potential is higher than for the platinum cathode on account of the higher "over-voltage" necessary to liberate hydrogen.

According to calculations made by the author, the variations of electrode potential with current density observed by Haber (compare Abstr., 1900, i, 281; Russ. Abstr., 1903, ii, 631) cannot be explained as the result of concentration changes at the cathode. H. M. D.

Anodic P.D.-Current Curve for Hydrochloric Acid at Platinum Electrodes. ROBERT LUTHER and FRANCIS J. BRISLEE (*Zeit. physikal. Chem.*, 1905, 50, 595—601. Compare Abstr., 1903, ii, 708).—A reply to Bose's criticism (Abstr., 1904, ii, 697). J. C. P.

Electrical Conductivity of Ethereal Solutions of Phosphoric Acid. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 37, 1282—1288).—Ethereal solutions of phosphoric acid possess considerable conductivity. An aqueous 87 per cent. solution of the acid has only three times as great a conductivity as the ethereal solution of corresponding concentration; at higher concentrations, the difference becomes still less. With diminution of the concentration, the conductivity in ethereal solution falls much more rapidly than in aqueous solutions. A similar rapid fall in conductivity is observed on diluting other non-aqueous solutions, and it remains an open question what concentration should be employed in estimating the dissociating power of a solvent. The molecular conductivity diminishes continuously as the concentration diminishes. With rise of temperature, the specific conductivity increases. The considerable development of heat occurring on dissolving phosphoric acid in ether and transforming the 90 per cent. solution to the crystalline condition at 25° may be an indirect indication of the existence of a chemical compound of ether with phosphoric acid. T. H. P.

Electrical Conductivity and other Properties of Sodium Hydroxide in Aqueous Solution, as elucidating the Mechanism of Conduction. WILLIAM ROBERT BOUSFIELD and THOMAS M. LOWRY (*Proc. Roy. Soc.*, 1904, 74, 280—283).—The conductivity of sodium hydroxide solutions, touched on in an earlier paper (Abstr., 1903, ii, 52), has been further studied. The conductivity-temperature curve exhibits an inflection (see *loc. cit.*) between 0° and 100° only in the case of solutions which are moderately dilute. The temperature of inflection varies regularly with the sodium

hydroxide concentration, from 48° for a normal (4 per cent.) solution to 100° for a 30 per cent. solution. When the sodium hydroxide solutions are very dilute or concentrated, no inflection occurs in the conductivity-temperature curve, and there is a marked parallelism between the change of conductivity and the change of viscosity with temperature. The inflected conductivity-temperature curves can be represented by the equation $K_t = K_o + at + \gamma(t - T)^3$, where T is the temperature of inflection, but the more general formula $K_t/K_o = \rho_t/\rho_o(1 + bt)^n e^{-at}$ is applicable to conductivity-temperature curves of all kinds. With the help of this formula, it is possible to make some approximation to resolving the two opposing influences (decay of ionisation and increase of ionic mobility with rising temperature) which determine the form of the conductivity-temperature curve.

The conductivity-concentration curve for sodium hydroxide solutions at 18° is similar to that given by Kohlrausch. The maximum conductivity at this temperature is 0.3490 (Kohlrausch's value = 0.3462) in a 15 per cent. solution. At higher temperatures the maximum conductivity is greater, rising to 1.4 at 100°, and occurs in more concentrated solutions.

The densities of sodium hydroxide solutions of different concentrations have been very carefully determined, the plan being to start from a large weighed quantity of sodium and to convert this quantitatively into the hydroxide. Eleven determinations, made with six different standard solutions, gave as the density of a 50 per cent. solution the value 1.5268, with an average error of 0.0001. The other solutions, the densities of which were to be determined, were prepared by diluting the strong standard solution. Such a density-concentration table having been drawn up, it is possible to deduce the concentration of any given sodium hydroxide solution more accurately from its density than from a titration of the solution. The variation of density with temperature becomes simpler in character as the concentration of the solution studied increases. Thus, when the equation $\rho_t = \rho_o + at + \beta t^2 + \gamma t^3$ is taken to represent the influence of temperature on the density of water and aqueous sodium hydroxide solutions, γ vanishes when the concentration of 12 per cent. of alkali is reached, and β vanishes at 42 per cent. concentration.

The viscosity of a 50 per cent. sodium hydroxide solution is about 70 times that of water. The influence of this factor on the ionic mobility may be to some extent eliminated by dealing with the ratio of molecular conductivity to fluidity. The molecular conductivity of sodium hydroxide solutions decreases with increasing concentration, but the foregoing ratio, termed the "intrinsic conductivity," falls to a minimum at about 8 per cent. sodium hydroxide and then rises, attaining at 50 per cent. concentration a value considerably greater than that found for the most dilute solutions. This is associated with the fact that liquid caustic soda is an electrolyte, and in concentrated solutions the caustic soda probably conveys the current partly as such.

The molecular volume of sodium hydroxide in dilute aqueous solution has a large negative value, a litre of water dissolving 140 grams at 0°, 100 grams at 18°, or 60 grams at 50°, without

increasing in volume. The molecular volume does not increase continuously with rising temperature, but reaches a maximum at about 70°. In a 50 per cent. solution, however, the temperature has little effect on the molecular volume. J. C. P.

Electrolysis with Alternating Currents. Passivity of Metals. MAX LE BLANC (*Zeit. Elektrochem.*, 1905, 11, 8—10).—Remarks on papers by Brochet and Petit (this vol., ii, 27) and by Sackur (Abstr., 1904, ii, 802). T. E.

Electrolysis with Alternating Current. CARLO ROSSI (*Chem. Centr.*, 1905, i, 61; from *L'Indust. Chim.*, 1904, 6, 333—335. Compare Le Blanc and Schick, Abstr., 1904, ii, 229).—Solutions of potassium chlorate acidified with sulphuric acid exhibit complicated phenomena when subjected to the action of an alternating current between copper or iron electrodes. The copper electrodes become coated with cuprous chloride, copper dissolves, and a bluish-green basic chlorate, $\text{Cu}(\text{ClO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, separates from the solution. When a direct current is used, cuprous chloride is formed at the anode, together with smaller quantities of basic chlorate and chloride; the solution, from which a complex mixture of cupric hydroxide, cupric oxide, copper, and cupric chloride separates out, does not contain dissolved copper. It is supposed that the copper passes into solution at the anode as cuprous ion, which reduces the chlorate, cupric copper being then precipitated by the alkali formed at the cathode. The non-reversibility of the change at the electrodes when alternating currents are used is probably due to the rapid removal of the cuprous ions in this manner. When, on the other hand, the potassium chlorate is replaced by sodium chloride, the alternating current dissolves very little copper. With iron electrodes, similar phenomena were observed. H. M. D.

Determination of the Electrochemical Equivalent of Silver. G. VAN DIJK (*Arch. Néerland.*, 1904, ii, 9, 447—525. Compare Abstr., 1904, ii, 255).—The present paper gives detailed descriptions of the methods and apparatus employed in the determination of this constant, the substance of the results having been already published (*loc. cit.*). An investigation into the influence of the form and manipulation of the voltameter on the value of the equivalent has also been made, and the author considers that the value of the equivalent is best represented by 0.011180. T. A. H.

Electrolytic Solution of Platinum. RUDOLF RUER (*Zeit. Elektrochem.*, 1905, ii, 10—12).—The author considers that his theory of the dissolution of platinum by alternating currents (Abstr., 1903, ii, 407) gives a much more satisfactory explanation of the phenomena than that advanced by Brochet and Petit (this vol., ii, 27 and 28). Several new experiments are described in which platinum anodes are polarised for a few seconds and then left exposed to a solution of sulphuric acid containing ferrous sulphate or sulphur dioxide for a few

seconds. Considerable quantities of platinum are dissolved, which would be quite inexplicable on the theory of Brochet and Petit, but is quite in accordance with that of the author. T. E.

Theory of Amphoteric Electrolytes. II. JAMES WALKER (*Proc. Roy. Soc.*, 1904, 74, 271—280).—The correction of a slight error in the calculations of the earlier paper (Abstr., 1904, ii, 309) leads to a still better agreement between the theoretical and experimental values of the conductivity for the aminobenzoic acids.

Formulae are deduced connecting the concentrations of the various components in the solution of an amphoteric electrolyte which is largely ionised. From a consideration of these formulae, it appears that the non-ionised proportion is unaffected by a simultaneous change of $1/k_a$, k_b , and v in the same ratio [k_a = dissociation constant of the electrolyte as acid, k_b = dissociation constant of the electrolyte as base, v = dilution]. This result is of importance in dealing with any series of amphoteric electrolytes for which the product $k_a.k_b$ is a constant. Here it may be shown that as k_a diminishes and k_b increases, the total ionisation falls off rapidly at first, then more slowly, until over a considerable range it is practically constant at the minimum value actually reached when $k_a = k_b$. The further increase of k_b and decrease of k_a is accompanied by corresponding changes in the ionisation until finally the electrolyte under consideration acts really as a simple base.

The author's theory has been further tested with satisfactory results in the cases of cacodylic acid (see Johnston, Abstr., 1904, i, 984) and asparagine. From Winkelblech's values of k_a and k_b for asparagine (Abstr., 1901, ii, 370), the molecular conductivity at $v = 16$ is calculated in good agreement with an actual determination, for which specially purified water and asparagine were employed.

The acidic or basic ionisation of an amphoteric electrolyte increases the freezing point depression, whereas the "saline" ionisation does not. In conjunction with the conductivity, the cryoscopic method should give useful results with soluble electrolytes which are largely ionised. J. C. P.

Contact Electrification and Colloidal Solutions. JEAN PERRIN (*J. Chim. phys.*, 1904, 2, 601—651).—The phenomenon of electric osmosis was first observed by Reuss, and subsequently investigated by Wiedemann, who showed that in a given liquid the loss by electric osmosis across a diaphragm varies with the current, is proportional to the cross section of the diaphragm and independent of its thickness. In the case of capillary tubes, Quincke showed that the transference is proportional to the square of the diameter, and also showed that some substances exhibit osmosis in the reverse sense. Quincke sought to explain the phenomenon by the existence of a double electrified layer at the walls. The tangential force of the field causes motion of the liquid layer and, hence, by friction, of the inner mass of liquid also, and Helmholtz proved that this explanation was in accord with the quantitative results. This explanation also holds for the *E.M.F.* of filtration and leads to the result that if a liquid filters under pressure across a given diaphragm the *E.M.F.* is proportional to the pressure and that this ratio depends

solely on the liquid, being independent of the thickness of the diaphragm or of the diameter of its pores. From observations of either the electric osmosis or the *E.M.F.* of filtration, determination may be made of the difference of potential between the liquids and walls. Similar reasoning also explains the motion of small suspended solids in the opposite sense. In the author's own experiments, although the diaphragm was varied and the field taken to 90 volts per cm., no osmosis was observed for chloroform, ether, petroleum, benzene, turpentine, or carbon disulphide, whilst with all diaphragms and in a field of 10 volts per cm. osmosis was readily found for water, ethyl alcohol, methyl alcohol, acetone, acetylacetone, and nitrobenzene. He hence concludes that electric osmosis is only easy in the case of liquids of high specific inductive capacity, that is, for ionising liquids, whilst low viscosity is also necessary. The influence of traces of dissolved electrolytes was then investigated, and it was found that powdered carbon becomes positively charged in slightly acidified water, and negatively in water rendered feebly alkaline. Similar results were obtained when anhydrous chromium chloride and other insoluble solids were used in place of carbon. The results are sometimes masked by a slight solubility of the compounds employed, but the results indicate the following general rule. The potential of any wall in an aqueous solution is always raised by the addition of a univalent acid to the solution and lowered by the addition of a univalent base. This influence is ascribed to the hydrogen and hydroxyl ions, other univalent ions having comparatively little influence. The great effect of these ions may possibly be due to a small diameter or sphere of molecular attraction. Polyvalent ions appear to diminish the electrification, the addition of sulphuric acid lowering the effect due to hydrochloric or nitric acids. The result is still more marked with trivalent or quadrivalent acids. This action may occasionally be of service in indicating the existence of polyvalent ions in solution. It seems probable also that a study of the laws of contact electrification may provide a means for evading or inducing the dragging down of soluble matter by precipitates. L. M. J.

Recent Investigations bearing on the Theory of Electrolytic Dissociation. LOUIS KAHLBERG (*Trans. Faraday Soc.*, 1905, 1, 42—53).—Experimental observations made by the author in connection with the properties of aqueous and non-aqueous solutions are summarised. Their bearing on the theory of solution and of electrolytic dissociation is discussed, and the conclusion is drawn that these theories are untenable.

No general agreement between the values of electrolytic dissociation as calculated from the conductivity, and from the vapour pressure, boiling point, or freezing point, has ever been established. Whereas Arrhenius's theory requires that the molecular conductivity shall always increase with dilution, cases are known where it diminishes or remains practically constant. The Nernst-Thomson rule, which ascribes the cause of dissociation to the high specific inductive capacity of the solvent, is not confirmed by later experiments.

The additive properties of solutions of electrolytes, which are

frequently regarded as evidence in favour of the dissociation theory, really form no argument, for in the case of pure liquids additive relationships are known to exist, for example, in the case of molecular volume and of molecular refractive power.

The theory refers the colours of solutions, say, of copper, nickel, and cobalt salts, to the ions, but non-conducting benzene solutions of the oleates of these metals are also blue, green, and red respectively, and the red cobalt solution turns blue on heating, just like the aqueous solutions.

Instantaneous reactions cannot be ascribed to ions, for non-conducting benzene solutions of hydrochloric acid and of copper oleate precipitate copper chloride practically instantaneously.

The behaviour of acids towards metals in non-aqueous solutions is not in accord with the assumption that the substances owe their characteristic properties to hydrogen ions, for non-conducting solutions of trichloroacetic acid in allylthiocarbimide attack dry magnesium rapidly and decompose the dry alkali carbonates.

Thermal data offer difficulties also, and the fact that Ostwald's dilution law holds good for certain organic acids in aqueous solutions is not of general significance. The essential electrolytes do not fit in with the law of mass action in aqueous solution, and in non-aqueous solvents it has yet to be shown that the mass action law is applicable. These and other facts lead the author to conclude that Arrhenius's dissociation theory is useless and misleading.

An acceptable theory of solution must not differentiate between the processes of solution and chemical action. A careful consideration of facts shows that these are "identical in character, and chemical compounds are merely the cleavage pieces of solutions placed under special stress or duress represented by the so-called purifying processes." The process of solution thus represents the general case of interaction of substances, union resulting when the specific attraction between them is, under the existing conditions, sufficient to cause a fusion or blending of their masses. In the further investigation of solutions, the most concentrated should receive first consideration, the dilute solutions only appearing as limiting cases. By means of vapour pressure, freezing point, and conductivity measurements carried out systematically on these lines, it should be possible to elaborate a theory of solutions on the basis of chemical affinity acting between solvent and solute.

H. M. D.

Ionisation in Flames. PIERRE MASSOULIER (*Compt. rend.*, 1905, 140, 234—236).—Using the flame of burning ether instead of coal gas, the author has measured the conductivity of a flame by Townsend's method (compare Abstr., 1901, ii, 221) at a lower temperature than that employed by Wilson (Abstr., 1899, ii, 722) or Moreau (Abstr., 1903, ii, 125, 196), and finds, contrary to the experience of these investigators, that the electrodes play only a secondary part in the experiment. Experiments are in progress to determine if the ionisation which is the cause of the conductivity of the flame is of chemical origin or merely due to the dissociation of the molecules at the high temperature.

M. A. W.

The Ions of the Atmosphere. P. LANGEVIN (*Compt. rend.*, 1905, 140, 232—234).—The author has extended his investigations on ionised gases (compare Abstr., 1902, ii, 301; 1903, ii, 263, 587) to the ions in the atmosphere at the top of the Eiffel Tower and finds that in addition to the ordinary ions having a mobility of 1.5 cm. for one volt per centimetre there are others having a mobility several thousand times smaller, and of the same order as those observed by Townsend in freshly prepared gases (Abstr., 1901, ii, 221) and by Bloch in the ions of phosphorus (Abstr., 1903, ii, 206; 1904, ii, 117; this vol., ii, 72); but the electric charge of the latter ions is fifty times as great as that of the ordinary ions.
M. A. W.

Registration of the Ions in the Atmosphere. P. LANGEVIN and M. MOULIN (*Compt. rend.*, 1905, 140, 305—307).—An arrangement for the automatic registration of the ionic condition of the atmosphere is described. By means of a small water turbine or electro-motor, a current of air is made to pass through a cylindrical condenser charged to constant potential, an electrode within the cylinder being connected with one of the quadrant pairs of a Curie electrometer. The air then passes through a meter, or anemometer, which sets in action a clockwork mechanism at intervals corresponding with the passage of a definite volume of air through the apparatus. For a description of the mechanical arrangements, by means of which this apparatus makes it possible to have the concentration of both positive and negative ions recorded automatically two or three times per hour, the original must be consulted.
H. M. D.

Cause of the Ionisation of Air in Contact with Phosphorus. EDGAR MEYER and ERNST MÜLLER (*Chem. Centr.*, 1905, i, 61—62; from *Verh. Deut. Phys. Ges.*, 1904, 2, 332—336).—The object of these experiments was to determine whether the ionisation of the air in contact with oxidising phosphorus is due to the light emitted in the process or to the oxidation itself. In presence of substances such as chlorine, ether, and turpentine, which inhibit the glowing of phosphorus, there is no oxidation and no ionisation, so that these experiments furnish no information. If phosphorus is allowed to oxidise in thin-walled quartz vessels which are transparent to ultra-violet radiation, no ionisation of the air can be detected. Examination of the spectrum of the radiation emitted by phosphorus undergoing oxidation shows it to be free from ultra-violet rays. The ozone produced in the oxidation cannot be the cause of the enormous conductivity imparted to the air; after removal of the ozone, the air retains its conducting power.
H. M. D.

High Temperature Measurements. THOMAS GRAY (*J. Soc. Chem. Ind.*, 1904, 24, 1192—1197).—The author gives a description of his own experience with various types of pyrometer.

The calorimetric method, using an iron cylinder, gives results which are usually within 10° of the truth at temperatures not exceeding about 1000°.

Several forms of direct reading and registering thermo-electric

pyrometers are described; calibration is most conveniently and accurately effected by direct comparison with a standard couple, the *E.M.F.* being measured by means of a potentiometer, but it may also be carried out by means of the boiling point of sulphur, the melting point of sodium carbonate (852°), and that of potassium sulphate (1066°). Convenient methods of working are described together with the precautions needed to ensure accuracy.

The platinum resistance thermometer is more sensitive and accurate than the thermo-element, but it is more easily damaged by contact with furnace gases if its protecting porcelain tube breaks, and it is more difficult to repair and restandardise.

The Wanner optical pyrometer is described: the light from the hot substance and the light from a small incandescent lamp pass through the same train of prisms (only the red rays being used for comparison) and then through a Nicol prism. By means of a double prism and lens of special construction, the extraordinary ray corresponding with the one source of light and the ordinary ray corresponding with the other are focussed together on a slit in the eye-piece; they are therefore polarised at right angles to each other, and the rotation of a Nicol prism in the eye-piece makes it possible to diminish the brightness of one and increase that of the other until they appear of equal brightness. The temperature is then obtained from the amount of rotation required. The great advantage of a pyrometer of this form is that no part of it is exposed to the high temperature, and therefore the frequent repairs and restandardisations needed with other pyrometers are avoided. T. E.

New Laboratory Burners and their Adaptation to the Production of High Temperatures. GEORGES MÉKER (*Bull. Soc. chim.*, 1905, [iii], 33, 210—215).—The burners are of the usual air-gas type, but the gas enters the chimney through an injector of special form, and the chimney is capped by a network of partitions of square section. This network presents a large cooling surface and so diminishes the tendency to "strike back." At the same time, it breaks up the air-gas stream, producing a large number of small jets which unite above to form an intensely hot, homogeneous flame. A laboratory burner of this type in action is figured in the original, which also gives particulars of the temperatures obtainable with these burners working under different conditions. T. A. H.

New Regulator for Thermostats. OCTAVE DONY-HÉNAULT (*Zeit. Elektrochem.*, 1905, 11, 3—5).—In the well-known Ostwald form of regulator, toluene cannot be used in the bulb which is placed in the thermostat because it creeps between mercury and glass and so causes a constant rise of temperature. This is avoided by making the part of the regulator which is outside the bath in the form of a double U-tube, connecting the toluene bulb to the top of the middle bend, and placing a layer of salt solution between it and the mercury. When the temperature of the air is constant, the temperature of the thermostat varies less than 0.001° ; the influence of fluctuations of the external temperature is diminished by making the volume of the

external tubes small in comparison with that of the immersed toluene bulb.

T. E.

Vaporisation of Solid Substances at the Ordinary Temperature. CONSTANTIN ZENGELIS (*Zeit. physikal. Chem.*, 1904, 50, 219—224).—When silver leaf is suspended over a layer of a metallic oxide in a closed vessel, the leaf, after a longer or shorter interval, begins to assume a yellow colour, and traces of the metal originally present in the oxide may be detected in the silver. In some cases, the increase in weight of the silver can be determined. The oxides found to act in this way were those of copper, zinc, iron, chromium, manganese, lead, cobalt, uranium, molybdenum, arsenic, and antimony. The action is favoured by partial exhaustion of the containing vessel, by the presence of moisture and of a reducing substance such as hydrogen or alcohol vapour. Comparative experiments with nickel, copper, and aluminium foil led to negative results, but gold leaf exposed to zinc oxide for six months was found to contain a trace of zinc. Other substances which melt only at a high temperature may be similarly shown to vaporise at the ordinary temperature; for example, sulphur, selenium, lead, copper, red phosphorus, tin, antimony and arsenic sulphides, iron, copper, and chromium hydroxides, copper carbonate, zinc chloride, and lead iodide. That such substances vaporise may be shown also by other methods: thus, if a watch-glass containing potassium ferrocyanide solution is kept along with copper or copper oxide in a closed vessel, the ferrocyanide gradually turns to a brownish-red colour.

J. C. P.

Molecular Weight Determination by the Rise of the Boiling Point in Cathode Ray Vacuum. FRIEDRICH KRAFFT and PAUL LEHMANN (*Ber.*, 1905, 38, 242—253. Compare Abstr., 1896, ii, 89, 464, 635; 1899, ii, 464).—In previous papers, it was established that the boiling point of high molecular liquids in the vacuum of the cathode light depended on the height of the vapour column above the liquid, and also on the molecular weight of the substance. A number of improvements have been introduced into the apparatus, for which the original should be consulted, among the most important being an arrangement allowing the thermometer to be moved so that the temperature at any position from immersion in the liquid to the very top of the column of vapour can be read at will. The work performed by each layer of vapour in raising up that over it causes an absorption of heat, so that in the case of mercury the temperature falls from 174° in the liquid to 152° at the top of the column of vapour 195 mm. high; a difference of 22°.

The difference of these two temperatures has been determined for various substances: in the case of palmitic and lauric acids and mercury, the differences observed, namely, 28·4°, 22·2°, and 22° respectively, are exactly proportional to the molecular weights. This relationship has been satisfactorily tested for a number of substances.

The method has been extended to the metals, the experiments being carried out in quartz vessels. Cadmium showed a fall of 5° for a

column of 80 mm. of vapour, zinc a fall of 3° , and lead one of $2-3^{\circ}$, these figures being in agreement with their molecular weights.

E. F. A.

Lowest Temperature of Evaporation of Metals in the Vacuum of the Cathode Light. FRIEDRICH KRAFFT and LUDWIG BERGFELD (*Ber.*, 1905, 38, 254—262. Compare Demarçay, *Compt. rend.*, 1882, 95, 183).—Attention has been paid to the accurate determination of the temperature at which metals heated in the vacuum of the cathode light first begin to evaporate. The experiments were performed in a horizontal tube 25 cm. long, connected at one end to the pump and cooled receiver, whilst the other was surrounded by a mantle in which the heating fluid was circulated; in some cases, a quartz tube was employed. In this way, the temperature of evaporation of cadmium was determined to be at 156.5° , silver at 680° , and similarly for a number of metals. For the details, the original should be consulted.

E. F. A.

Boiling Point in Vacuum; a New Constant and its Meaning. FRIEDRICH KRAFFT (*Ber.*, 1905, 38, 262—266. Compare preceding abstracts).—It is pointed out that mercury begins to evaporate at about -40° , boils in vacuum at 155° , and under the ordinary pressure at 357° . The interval (195°) between the commencement of evaporation and the point at which the substance boils in vacuum, during which work is done in overcoming gravity, is approximately equal to that (202°) between the boiling point in vacuum and at the ordinary pressure, during which work is done in overcoming the pressure of the atmosphere. The same relationship holds for all the metals experimented with; as a general rule, as much heat is required, starting from the beginning of evaporation, to overcome the resistance of gravity as is further required to overcome the pressure of the atmosphere, or, in other words, gravity and atmospheric pressure are equivalent.

The results are summarised as follows, column I giving the temperature at which evaporation begins in the vacuum, column III the boiling point in the vacuum, and column V the boiling point under 760 mm. pressure.

	I.	Diff.	III.	Diff.	V.
Mercury	-40°	195°	155°	202	357°
Cadmium	156	294	450	299	749
Zinc	184	366	550	370	920
Potassium	63	302	365	302	667
Sodium	98	320	418	324	742
Bismuth	270	723	993	707	1700
Silver	680	680	1360	680	2040

E. F. A.

Conductivity of Nitrogen Dioxide for Heat. C. FELICIANI (*Chem. Centr.*, 1905, i, 331; from *Physikal. Zeit.*, 1905, 6, 20—22).—The conductivity of nitrogen dioxide was examined by the method of cooling at different pressures and temperatures (18° to 131°). Allowance being made for convection, there is an increase in the con-

ductivity at all pressures at 65°, followed by a decrease to a minimum and a second increase between 120° and 130°.

The conductivity increases with the pressure, and the conductivity and dissociation curves follow similar courses. Up to 90° and for pressures of not less than 60 mm., the conductivity of nitrogen dioxide is larger than that of any non-dissociating gas examined previously.

Magnanini's numbers, used by Nernst (*Boltzmann Festschrift*, 1904), are not quite trustworthy. The value for the conductivity of a mixture of NO_2 and N_2O_4 cannot be taken as equal to that of CO_2 , the author obtaining somewhat higher values than those calculated by Nernst.

G. D. L.

Heats of Combustion of Atoms and Molecules. LAWRENCE J. HENDERSON (*J. Physical Chem.*, 1905, 9, 40—56).—From consideration of the values of the heats of combustion of a number of substances, the author shows that the same substitution affects the heat of combustion to different extents. Thus, the substitution of $\cdot\text{OH}$ for $\cdot\text{H}$ diminishes the heat of combustion by 40 cal. when it converts a paraffin hydrocarbon into a primary alcohol, but by 72 cal. when it converts an aldehyde into an acid. These values are not, however, absolutely constant, but the differences vary in a regular way, and the author considers that every atom of a molecule, in a degree dependent upon its position, influences the heat of combustion of every other atom of the molecule, whether or not it is united to that atom.

L. M. J.

Depression of the Freezing Point in Dilute Solutions of Highly Dissociated Electrolytes, HANS JAHN (*Zeit. physikal. Chem.*, 1904, 50, 129—168. Compare Abstr., 1900, ii, 707; 1901, ii, 491, 592).—With an apparatus similar to that used by Hausrath (Abstr., 1903, ii, 61), the author has very carefully determined the freezing points of dilute solutions of lithium, sodium, potassium, and caesium chlorides, sodium and potassium bromides. Lithium chloride is peculiar in that the molecular depression exhibits a minimum, whilst in all the other cases the molecular depression increases regularly as the concentration decreases. Δ , the freezing point depression, and N , the number of gram equivalents of salt in 1000 grams of water, are connected by the following equations, which give numbers in very good agreement with experiment, N having values from 0.1 downwards: (1) for potassium chloride, $\Delta = 3.5605N - 0.98196N^2$; (2) for sodium chloride, $\Delta = 3.5582N - 0.87452N^2$; (3) for lithium chloride, $\Delta = 3.6116N - 0.8857N^2$. The values for the ionic concentration (n_1), deduced from the freezing point depression, agree very well with those deduced from the conductivity in the cases of sodium and potassium chlorides; for lithium chloride, the conductivity method gives smaller values, for caesium chloride and potassium bromide, greater values of n_1 , than the freezing point method. Even sodium and potassium chlorides, however, are very far from following the formula $n_1^2/(N - n_1) = \text{const.}$, and the author concludes that the values of n_1 , based on the validity of the simple solution laws, are wrong. He further contends that the accepted values of μ_∞ are probably too high on account of hydrolysis

in very dilute solutions and the impurities of the water and the glass of the containing vessel. If 106.85 is taken as the value of μ_{∞} for sodium chloride instead of the usual 108.1, the dissociation equation given above is applicable in dilute solutions and the constant = about 0.160. A similar value is found, independent of the dilution, when n_1 is deduced from the author's expanded formula for the freezing point depression (see Abstr., 1902, ii, 597). The *E.M.F.* of sodium chloride concentration cells may be calculated with the aid of the foregoing constant, and the values so found are in good agreement with experiment. Similar remarks apply to the other electrolytes studied. The attempt made in this paper to reconcile the dissociation theory with the laws of thermodynamics in the case of highly dissociated electrolytes leads, further, to the conclusion that the ionic mobility must increase with increasing concentration of the solution. It is necessary also to regard Arrhenius' formula $\alpha = \mu/\mu_{\infty}$ as valid only in very dilute solutions. J. C. P.

Specific Volume as the Determining Criterion of Chemical Combination in Metal Alloys. II. E. MAEY (*Zeit. physikal. Chem.*, 1904, 50, 200—218. Compare Abstr., 1901, ii, 655).—In the case of alloys where there is no chemical combination, the specific volume can be calculated by the mixture formula to within 1 per cent. of its true value. A greater deviation than this is due generally to the formation of a compound, or sometimes, if less marked, to that of solid solutions only. The specific gravity of a large number of alloys of different composition has been determined, and from the break in the curve obtained by plotting specific volume against composition it appears that in eight out of the thirteen binary alloys investigated chemical combination of the component metals takes place. The compounds thus indicated are Sb_3Zn_2 , Sb_2Cd_3 , SbAg_3 , SbCu_3 , AgZn_4 , AgCd_2 or AgCd_3 , CuCd_2 , AgHg . The existence of several of these has been indicated by other methods (compare, for example, Herschkowitsch, Abstr., 1898, ii, 582; Heycock and Neville, Abstr., 1897, ii, 245), but the exact formula adopted differs in some cases. With the combinations Zn—Hg, Cd—Hg, Cd—Zn, Bi—Zn, and Pb—Zn, there was no certain indication of the existence of a compound.

Stress is laid on the treatment of the specific volume, and not the specific gravity, as an additive property. J. C. P.

Vapour Pressure by Air-bubbling. EDGAR P. PERMAN (*J. Physical Chem.*, 1905, 9, 36—39).—Doubts regarding the accuracy of the method of air-bubbling for the determination of vapour pressure have been raised by Carveth and Fowler (Abstr., 1904, ii, 541). The author defends the method and quotes results obtained previously by himself to show that with sufficient care accuracy is obtainable, at any rate, in the case of water as solvent. He further raises objections to the methods employed by Carveth and Fowler in their experiments (compare Trans., 1903, 83, 1168). L. M. J.

Dissociation of Nitro-derivatives in Certain Solvents. III. GIUSEPPE BRUNI and B. SALA (*Gazzetta*, 1904, 34, ii, 479—485. Compare Bruni and Berti, Abstr., 1900, ii, 591 and 592).—Determinations of

the elevations of the boiling points of solutions of naphthalene, diphenyl, dibenzyl, and trichlorobenzene in acetonitrile give the mean value 17.3 for the molecular elevation of the boiling point of this solvent. The number given by Kahlenberg (*Abstr.*, 1902, ii, 310), namely, 14.39, is hence low.

In boiling acetonitrile, picric acid, picryl chloride [1:3:5-trinitro-2-chlorobenzene], 2:4:6-trinitrotoluene, trinitro-*p*-xylene, and dinitromesitylene all undergo a considerable amount of dissociation, whilst bromodinitromesitylene exhibits normal ebullioscopic relations. The behaviour of the last-named compound, in which the hydrogen atoms of the benzene nucleus are all substituted, is in accord with that of trinitromesitylene in formic acid solution (Bruni and Berti, *loc. cit.*).

In methyl-alcoholic solution, picryl chloride, trinitro-*p*-xylene, and dinitromesitylene all undergo dissociation. In boiling ethyl alcohol or acetone, however, picryl chloride gives perfectly normal molecular weights.

The theory put forward by V. Meyer (*Abstr.*, 1896, i, 419) to explain the dissociation of nitro-compounds supposes that, under the electro-negative action of the nitro-groups, one of the hydrogen atoms of the aromatic nucleus becomes capable of dissociation without the intermediate formation of *isonitro*-groups. To ascertain whether other electro-negative groups exert a similar influence to that of the nitro-group, the author has determined the molecular weight of *s*-trichlorobenzene in boiling acetonitrile and methyl alcohol. The numbers obtained are quite normal, showing that the power of exciting dissociation is a specific property of the nitro-group, and not a general one of all electro-negative groups.

T. H. P.

Diffusion of Salts in Solution. J. C. GRAHAM (*Zeit. physikal. Chem.*, 1904, 50, 257—272).—Vertical columns of salt solution and pure water of the same section are brought together, so that there is no initial mixing at the common surface. After some time, the salt concentration at various levels both above and below the common surface is determined. The author takes Fourier's series as the groundwork of his computations, and concludes from his experiments that the diffusion of salts follows the same laws as the conduction of heat. The diffusion constant for each salt is independent of the density of the solution and of the time during which diffusion has taken place. The salts employed in the author's experiments were the chlorides of sodium, potassium, ammonium, zinc, and manganese, the nitrates and carbonates of sodium and potassium, and ammonium sulphate. The results obtained indicate no evident connection between the value of the diffusion constant and the molecular weight. When sodium and potassium chlorides and sodium and potassium nitrates are allowed to diffuse in dilute hydrochloric acid and dilute nitric acid respectively instead of in pure water, slightly higher values are obtained for the diffusion constant.

J. C. P.

Diffusion of Electrolytes in Water. L. WILLIAM ÖHOLM (*Zeit. physikal. Chem.*, 1904, 50, 309—349).—The electrolytes studied were

the chlorides of lithium, sodium, and potassium, the hydroxides of sodium and potassium, potassium iodide, and hydrochloric and acetic acids. In all cases there was found a certain concentration below which the diffusion-coefficient increases as the solutions become more dilute. From the same point, the coefficient increases also with increasing concentration, and consequently exhibits a minimum, provided that the formation of complex molecules at higher concentrations does not mask the true variation of the diffusion-coefficient. The concentration at which the minimum occurs is different for different electrolytes.

The temperature-coefficient of the diffusion constant varies also with the electrolyte studied, and is equal to the sum of the temperature-coefficients of the osmotic pressure and the electric conductivity. The author's experiments are in harmony with Nernst's theory dealing with the calculation of diffusion-coefficients at infinite dilution (*Zeit. physikal. Chem.*, 1888, 2, 613) and with Arrhenius' views on the variation of the diffusion-coefficient with the dilution (*Abstr.*, 1892, 1265).

It is shown that the internal friction of the molecule is somewhat less than the sum of the corresponding quantities for the ions.

J. C. P.

Verification of a Recent Equation of Van der Waals.
JOHANNES J. VAN LAAR (*Arch. Néerland*, 1904, [ii], 9, 389—417. Compare Van der Waals, *Abstr.*, 1901, ii, 644).—I. *Variation of b in the Case of Hydrogen.*—Van der Waals has asserted (*loc. cit.*) that in the case of a diatomic gas the relationship $(b + b_0)/(v - b) = 1 - [(b - b_0)/(b_1 - b_0)]^2$ holds where b_0 is the least value of b (reached when the atoms are in contact) and b_1 its greatest value (obtained when the volume of the gas is infinitely great). Comparing the values of b calculated from this relationship with those deduced directly from Amagat's results, it is found that the two values only become concordant for pressures above 300 atmospheres at 0°, above 400 atmospheres at 100°, and above 250 atmospheres at 200°. Further, the critical constants calculated on the assumption that the values of b_0 and b_1 are independent of the temperature, as is implied by Van der Waals's hypothesis that the value of a is directly proportional to the absolute temperature, are not in good agreement with those determined experimentally, in particular there is lack of concordance in the calculated and observed critical volumes.

From his results the author draws the conclusion that $(b_0 - b_1)^2$ is proportional to the absolute temperature, b_1 being constant and b_0 variable, while a is independent of temperature.

II. *Specific Heats of Liquids at Low Temperatures.*—It is shown that specific heats at constant volume calculated from the relation $C_v = RT[2/T - 1/(v - b)(db/dT)_v + 1/(b - b_0)(d\{b - b_0\}/dT)_v]$, on the assumption that $b_1 - b_0 = \sqrt{\gamma T}$ (see above), are in good agreement with those determined experimentally. The concordance of the calculated and observed results for liquids affords a further proof that the variation in value of $(b_1 - b_0)$ with temperature is due to change in b_0 , b_1 remaining constant.

It is pointed out that for many diatomic and for some more complex substances the quotient of melting point by critical temperature, both being expressed on the absolute scale, is approximately 0.5.

T. A. H.

Validity of the Law of Corresponding States for Mixtures of Methyl Chloride and Carbon Dioxide. H. KAMERLINGH ONNES and C. ZAKRZEWSKI (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 285—290 and 377—382. Compare Abstr., 1904, ii, 807).—From a study of the conditions of coexistence, it appears that for mixtures of methyl chloride and carbon dioxide there are deviations from the law of corresponding states which become very marked for liquid densities and low temperatures.

J. C. P.

More Exact Equation of Condition for Gases. III. J. B. GOEBEL (*Zeit. physikal. Chem.*, 1904, **50**, 238—240).—A supplementary note to earlier papers (see Abstr., 1904, ii, 311, 706).

J. C. P.

Kinetics of the Nitration Reaction. HAAVARD MARTINSEN (*Zeit. physikal. Chem.*, 1904, **50**, 385—435).—The nitration of nitrobenzene to *m*-dinitrobenzene in concentrated sulphuric acid solution is shown by experiments at 0° and 25° to be a reaction of the second order, although the velocity-coefficient at 0° falls off slightly with the time, probably because part of the nitrobenzene undergoes sulphonation during the long time required for the experiments at the lower temperature. The velocity of nitration is more than trebled for a rise of 10°. The velocity varies also with the strength of the sulphuric acid used as medium, and reaches a maximum when the molecular ratio of sulphuric acid to water is about 1.0 : 0.7. The course of the change was followed by taking portions of the reaction mixture from time to time, and either extracting the nitro-compound with ether and determining the amount of stannous chloride oxidised by it, or estimating the amount of unconsumed nitric acid in a nitrometer.

The nitration of 2 : 4-dinitrotoluene or of *o*-, *m*-, and *p*-nitrobenzoic acids follows the course of a bimolecular reaction. The introduction of a methyl group in the nitrobenzene molecule increases the velocity of nitration. A carboxyl group has the opposite effect, but the extent of its influence depends on its position, and is lessened by converting the acid into ester. The introduction of a nitro-group diminishes the rate of nitration to a greater extent than the introduction of a carboxyl group. When *p*-nitroaniline is nitrated, two nitro-groups are introduced at nearly the same rate, and the reaction results in the formation of picramide. The rate of nitration of α -nitronaphthalene is greater than that of nitrobenzene.

The nitration of phenol in aqueous solution is a complicated autocatalytic reaction, the velocity increasing with increasing acid concentration, but decreasing with increasing phenol concentration. The velocity of nitration is increased markedly by the addition of potassium nitrate or sulphuric acid, to a less extent by the addition of sodium and strontium nitrates. Nitrous acid acts as a catalytic agent, and the autocatalytic character of the reaction is to be attributed to the production of this substance during the nitration process; the rate of

nitration and the rate of production of nitrous acid run parallel, and when the production of nitrous acid is prevented no nitration takes place, at least when the nitric acid concentration is not too great. Nitrosophenol increases the velocity of nitration, but its effect is almost independent of its concentration.

The nitration of *p*-cresol is very similar to that of phenol.

J. C. P.

Chemical Kinetics of the Benzoin Synthesis (Catalysis by Cyanide Ions). ERNST STERN (*Zeit. physikal. Chem.*, 1905, 50, 513—559. Compare Lapworth, *Trans.*, 1903, 83, 995).—The gradual conversion of benzaldehyde into benzoin in aqueous alcoholic solution under the influence of potassium cyanide may be followed by taking samples of the reaction mixture from time to time and estimating their reducing power with Fehling's solution. The change, for the first half of its course at least, and within certain concentration limits, is regular, and follows the course of a bimolecular reaction. The rate of change is further proportional to the concentration of the potassium cyanide, and a similar statement applies when other ionised cyanides are used; when, however, the $-CN$ group is in a complex, it is without influence. It thus appears that the reaction is one in which the catalytic agent is the cyanide ion. Free hydrocyanic acid and free alkali are without catalytic effect, although in certain circumstances they may give rise to secondary reactions. When the percentage of water in the aqueous alcohol is raised, the rate of change increases. The variation of the reaction velocity with temperature is in accordance with the usual law. The influence of benzaldehyde on the conductivity of an aqueous alcoholic solution of potassium cyanide is inappreciable at higher temperatures, but is considerable at 0° , and the experiments made in this connection indicate a reversible interaction between benzaldehyde and potassium cyanide. The various theories of the benzoin synthesis that have been advanced are discussed, and those which refer the synthesis solely or chiefly to the presence of alkali or hydrocyanic acid are regarded as discounted by the author's experiments.

J. C. P.

Mechanism of Ether Formation from Alkyl Haloid (or Halogen Dinitrobenzene) and Sodium Alkylxide. C. A. LOBBY DE BRUYN and S. TIJMSMA (*Zeit. physikal. Chem.*, 1904, 50, 436—442. Compare Hecht, Conrad, and Brückner, *Abstr.*, 1889, 931; 1890, 4, 327, 1046; de Bruyn and Steger, *Abstr.*, 1899, i, 744, 745; Nef, *Abstr.*, 1900, i, 4; Luloffs, *Abstr.*, 1902, i, 87; Burke and Donnan, *Trans.*, 1904, 85, 555).—To explain the peculiarities in the rate of formation of ethers as observed and discussed by the above-mentioned investigators, the authors suppose that the alkyl haloid is dissociated to a slight extent. This would account for the influence of added sodium haloid in lessening the rate of change. The fact that a velocity constant is obtained at all, in spite of the sodium haloid produced during the change, might be attributed to the formation of a compound between the ether and the sodium haloid, but some experiments made by the authors are unfavourable to this explanation. The reaction

mixture becomes more dilute with respect to alkyl haloid as the change proceeds, and possibly the consequent increase of dissociation of the alkyl haloid is exactly neutralised by the effect of the sodium haloid produced.

J. C. P.

Periodic Contact Catalysis. II. GEORG BREDIG and E. WILKE (*Chem. Centr.*, 1905, i, 64; from *Verh. Heidelberg Natur-hist. med. Ver.*, 1904, [N.F.], 8, 165—181. Compare Bredig and Weinmayr, 1903, ii, 279).—In strongly alkaline solution, hydrogen peroxide is rapidly and continuously decomposed in contact with mercury which acts catalytically. In acid solution, the mercury is slowly oxidised, whilst in feebly alkaline solution the action is of periodic character and oxygen is intermittently evolved. The best results are obtained when the concentration of the alkali is 10^{-3} to 10^{-4} gram-mols. per litre. The rate of intermittence increases during an experiment; it diminishes with fall of temperature, whilst rise of temperature beyond a certain limit causes the action to become aperiodic. The periodicity is also affected by pressure and by light.

When the mercury surface is made an anode or a cathode in contact with alkaline hydrogen peroxide solution, the periodic phenomena are still observable. The quantity of alkali necessary for the effect varies with the potential of the mercury. The effect is diminished by extremely small quantities of alkali chloride ($1/25000$ — $1/50000$ mols. per litre), probably in consequence of the formation of a thin layer of mercurous chloride. Nitrates are without action; sulphates diminish the pulsation when added in larger quantity.

The character of the pulsations has been studied in a similar manner to that adopted in Ostwald's experiments on the solution of chromium in acids. The regular curves obtained indicate a slow continuous change during the active period, and a rapid fall when the maximum has been reached. The form of these curves is altered when any foreign substance is added to the solution. The addition of colloids causes the apices of the curves to assume a much more pointed character. The action of the colloids probably consists in altering the rate of formation and the stability of the oxide layer on which the periodic phenomena depend.

H. M. D.

Influence of Metals on the Hydrolysis of Sucrose. RUDOLF VONDRÁČEK (*Zeit. physikal. Chem.*, 1905, 50, 560—566).—The influence of platinum in compact form on the rate of inversion of sucrose is very slight (see also Raýman and Sulc, *Abstr.*, 1897, ii, 136; Lindet, *Abstr.*, 1904, i, 293; Plzák and Hušek, *ibid.*, ii, 391). Fresh platinum black, however, has a marked accelerating effect, but the author has observed that a sample of platinum black once used to induce inversion is without effect on a second sucrose solution. Drying at 150° restores its activity (compare Purgotti and Zanichelli, *Abstr.*, 1904, ii, 329), which is therefore probably due to the presence of oxygen. When a sucrose solution is heated for a short time with platinum black and then filtered, the inversion proceeds according to the formula for a unimolecular reaction, the inverting agent being the oxidation products of the sugar. Indeed, evidence of the presence of

H⁺ ions in a sucrose solution treated with platinum black can be deduced from measurements of the conductivity. J. C. P.

Solubility of some Sparingly Soluble Salts in Water at 18°. FRIEDRICH KOHLRAUSCH (*Zeit. physikal. Chem.*, 1904, 50, 355—356. Compare Abstr., 1903, ii, 528).—Values for the solubility deduced from the conductivity of the saturated solutions are here recorded for a number of sparingly soluble salts. The list has been prepared for the new edition of Landolt and Börnstein, and is almost complete, although some points still remain to be examined, such as the influence of temperature on the solubility. The temperature for which the present numbers are valid is 18°, except in the cases of silver bromide and iodide, where the temperature is 21°. In the following list, the first number after the name of the substance is the specific conductivity of the saturated solution, the second, in brackets, is the weight in milligrams of the substance per litre of the saturated solution: barium fluoride, 1530 (1630); strontium fluoride, 172 (117); calcium fluoride, 40 (16); magnesium fluoride, 224 (76); lead fluoride, 431 (640); silver chloride, 1.25 (1.6); silver bromide, 0.075 (0.107); silver iodide, 0.002 (0.0035); thallium chloride, 1514 (3040); thallium bromide, 192 (420); thallium iodide, 22.3 (56); mercurous chloride, 1.2 (2); mercuric iodide, 0.2 (0.4); silver iodate, 11.9 (40); lead iodate, 6.2 (19); barium sulphate, 2.4 (2.3); strontium sulphate, 127 (114); gypsum, 1885 (2040); lead sulphate, 32.4 (41); barium chromate, 3.2 (3.8); silver chromate, 18.5 (25); lead chromate, 0.1 (0.2); barium oxalate ($\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 78.3 (86); strontium oxalate (SrC_2O_4), 54 (46); calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), 9.6 (5.6); magnesium oxalate ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 200 (300); zinc oxalate ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 8 (6.4); cadmium oxalate ($\text{CdC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$), 27 (33); silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$), 25.5 (35); lead oxalate (PbC_2O_4), 1.3 (1.5).

In some of the foregoing numbers, the last number is uncertain.

J. C. P.

Molecular Attraction (3). J. E. MILLS (*J. Physical Chem.*, 1904, 8, 593—636).—In the two previous papers (Abstr., 1902, ii, 596; 1904, ii, 642), the equation $L - E = k(\sqrt[3]{\bar{d}} - \sqrt[3]{\bar{D}})$ was applied to 21 different substances employing values for L calculated from dp/dT , the latter ratio being obtained not from vapour pressure observations themselves, but from these results smoothed by Biot's formula. The constant b of the equation $p = bT + a$, proposed by Ramsay and Young, is a dP/dT , and at the critical temperature is identical with the dP/dt of the thermodynamical equation. It was found that by use of b instead of the Biot dP/dT better agreement was obtained at the critical temperature in those cases where the accord had previously been unsatisfactory. It was also found that in the cases where divergencies in the values of the constant occur, irregularities also occur in the curve representing PV against temperature. The author gives a number of curves for $L - E$ against $\sqrt[3]{\bar{d}} - \sqrt[3]{\bar{D}}$, which indicate very clearly the agreements of the constants. Three equations are now

available for calculating latent heats. (1) The thermodynamical $L = T/J.(V - v)dP/dT$; (2) $L = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) + E$, and (3) Crompton's equation, $L = 2RT \log d/D$. The values of L for the different substances examined are calculated from these equations; it is seen that as a rule Crompton's equation at low temperatures gives high results, but at high temperatures gives results in better accord with (2) than those calculated by equation (1). For high temperatures, therefore, Crompton's equation should prove of considerable value, as owing to the uncertainty in the values of dP/dT the values obtained thermodynamically are untrustworthy. Curves are given for the variation of internal latent heat with temperature; it is seen that all are concave towards the temperature axis, but no simple empirical formula could be obtained. From the equation previously given, the value of a in Ramsay and Young's expression may be calculated. In the case of isopentane, the value obtained is 159,400, the volume V being 4.266. Young obtained the value 157,880 at $V = 4.3$ from the drawn isochors, and 162,890 by calculation. It is shown also that at the critical temperature the following relations hold: (1) $P = dP/dT.T - 10,471\mu'/V^{4/3}$; (2) $dP/dT = 124,860/mV$, and (3) $m\mu'\sqrt[3]{d}/T = \text{constant}$. L. M. J.

Theory of Colloids. EDUARD JORDIS (*Chem. Centr.*, 1904, ii, 1683—1686; from *Mon. Sci.*, [iv], 18, 797—818. Compare Abstr., 1904, ii, 714).—According to the theory propounded, colloidal solutions do not differ essentially from ordinary solutions. A comparison of the properties of colloids with those of crystalloids indicates that no sharp line of demarcation can be drawn between the two classes. As yet a pure hydrosol has not been prepared, and it is probable that purification leads in all cases to the formation of a hydrogel. The hydrosols, therefore, are not pure substances, but are to be regarded as combinations which the author designates as "chemical colloids."

The process of neutralisation of acid and basic colloids, the precipitation of albumin by alkali halogen salts in acid and alkaline solution, the influence of concentration on the precipitation of colloids, the causes of hydrogel formation, the electrolysis of hydrosols, the different hypotheses relative to the structure of hydrogels, and many other points are discussed, for which the original must be consulted.

Incidentally the author divides the colloids into six groups according to their modes of formation. These are (1) precipitation by alkali, by hydrolysis, or by acids; (2) precipitation by hydrogen sulphide; (3) formation of halogen colloids from metallic hydrosols; (4) formation of complex substances such as Prussian blue; (5) reduction of salts of heavy metals; (6) electrical disintegration of metals under water.

H. M. D.

Solid Solutions and Isomorphism. GIUSEPPE BRUNI and A. TROVANELLI (*Gazzetta*, 1904, 34, ii, 349—357).—Thioacetic acid gives abnormally small freezing point depressions in acetic acid solution. Thioacetamide, on the other hand, gives depressions greater than the normal values in solution in acetamide (the constant of which was determined to be 36.3). In formamide (the freezing point constant of

which was found to be 38.5), thioacetamide gives normal depressions, showing that here the thioacetamide is not appreciably dissociated and that mixed crystals are not formed with acetamide. In urethane solutions, ethyl thiocarbamate gives depressions smaller than the normal values, whilst xanthamide or ethyl sulphocarbamate gives depressions slightly greater than the normal ones. Compounds of the aliphatic series containing the group $\text{:C}\cdot\text{SH}$ hence form solid solutions with the corresponding compounds containing the complex $\text{:C}\cdot\text{OH}$, but those with the grouping $\text{:C}\cdot\text{S}$ are not able to crystallise with the corresponding oxygen compounds.

Thiophenol exhibits normal cryoscopic behaviour in phenol solutions.

p-Fluoronitrobenzene gives depressions somewhat higher than the normal values when dissolved in *p*-chloronitrobenzene, the molecular freezing point depression for which is 108. This is the first observed case of isomorphism between fluoro- and chloro-organic derivatives.

T. H. P.

Decomposition of Hydrated Mixed Crystals. II. REINHARD HOLLMANN (*Zeit. physikal. Chem.*, 1905, 50, 567—594. Compare Abstr., 1902, ii, 446).—A theoretical paper. J. C. P.

Mixed Crystals in Systems of Three Substances. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1904, 50, 169—199).—A theoretical paper. J. C. P.

Method for the Determination of the Affinities of Acids Colorimetrically by means of Certain Vegetable Colouring Matters. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1905, 33, 46—59).—It is shown that dilute solutions of certain vegetable colouring matters can be used for determining the relative strengths of acids. The following materials have been found to contain colouring matters capable of employment for this purpose: the skin of the purple grape and of the wild grape (*Vitis vulpina*), the flowers of the red geranium, purple petunia, the scarlet sage (*Salvia fulgens*), and the red rose. The reagent is prepared by macerating the grape skins (or other material) with water, boiling, filtering, adding a small quantity of solution of egg albumin to clear the liquid, which is afterwards boiled and filtered. A current of sulphur dioxide is then passed into the liquid until the colour is almost discharged, and the excess of sulphur dioxide is removed by boiling, a little toluene being added as a preservative. The effect of various acids on the reagent has been studied, and it is found that the colouring matter is regenerated on the addition of an acid, the intensity of the colour varying according to the affinity of the acid.

On arranging the acids in order of their affinity as determined by this process, it is found that this order agrees closely with that obtained by Ostwald's methods.

It has not been found possible to exhibit the difference in strength between the very weak acids, such as acetic, propionic, and butyric acids, by this colorimetric method, but it is thought that possibly this may be effected by varying the concentration.

E. G.

Sixth Report of the Committee [of the German Chemical Society] for Fixing Atomic Weights. HANS LANDOLT, WILHELM OSTWALD, and OTTO WALLACH (*Ber.*, 1905, **38**, 13—22. Compare *Abstr.*, 1902, ii, 129; 1903, ii, 68; 1904, ii, 20).—This report deals with the replies to a circular addressed to the members of the International Committee relating to the basis of the atomic weights. Of the fifty-nine members, thirty-nine recorded their votes, and of these thirty-two were in favour of the exclusive publication of the table based on $O=16$, two were in favour of the table in which $H=1$, whilst five were in favour of both tables being given. The committee therefore proposes the exclusive use of the values based on $O=16$.

C. H. D.

Theory of Valency. RICHARD ABEGG (*Zeit. anorg. Chem.*, 1905, **43**, 116—121. Compare *Abstr.*, 1903, ii, 536; 1904, ii, 475).—A theoretical paper in which the following problem is discussed. If an uncombined polyvalent atom of an element is present in a system containing an amount of another element insufficient to form the compound corresponding with the lowest stage of combination, will one valency of the atom in question be concerned in the formation of the compound, or will all the valencies take a part? Although experience appears to favour the first alternative, the latter is considered to be the more correct, especially since the affinities of the different valencies of one atom have not all the same value.

A. McK.

Conception of Valency. RICHARD ABEGG and F. WILLY HINRICHSSEN (*Zeit. anorg. Chem.*, 1905, **43**, 122—124).—A criticism of the views of Billitzer (*Abstr.*, 1904, ii, 720), who considers that the valency of an element is a function of the temperature. The authors draw a sharp distinction between the valency of an element and its "affinity."

A. McK.

Hydration and Hardening. EDUARD JORDIS (*Zeit. Elektrochem.*, 1904, **10**, 938—940).—The views regarding the hardening of Portland cement and gypsum expressed by Rohland (this vol., ii, 19) are adversely criticised. The acceleration of the setting of cement by the addition of salts is not a catalytic process, since the salts added react with the cement and undergo permanent change.

T. E.

Siphon with a Mercury Valve. FERDINAND PILZ (*Chem. Centr.*, 1905, i, 133; from *Zeit. Landw. Vers.-Wes. Oesterr.*, **7**, 819).—The delivery tube is bent in a U-form, and is connected by a tube from the bottom of the bend with a pear-shaped glass bulb, which is attached by a ground glass joint and is capable of rotation. The bulb and U-tube contain mercury, and by rotating the bulb downwards the level of mercury is depressed, so that the liquid may pass the bend of the delivery tube.

The valve is designed for use with alkaline liquids, for which glass or rubber is undesirable.

G. D. L.

Inorganic Chemistry.

Hypochlorous Acid. III. Formation and Decomposition of Chloric Acid. JULIUS SAND (*Zeit. physikal. Chem.*, 1904, **50**, 465—480. Compare Abstr., 1904, ii, 612).—The slow liberation of chlorine at 70° in a solution containing potassium chlorate and hydrochloric acid has been quantitatively followed. It appears that the reaction is quinquemolecular, and that the rate of change at any moment is given by the equation $dx/dt = k[\text{ClO}_3'] \cdot [\text{H}']^2 [\text{Cl}']^2$. The velocity actually measured is probably that of the action $\text{ClO}_3' + 2\text{H}' + 2\text{Cl}' = \text{ClO}' + 2\text{HOCl}$, the hypochlorous acid then reacting instantaneously with hydrochloric acid to produce chlorine. The absolute value of k_{70} works out to 0.56×10^{-3} .

The action represented by the foregoing equation is reversible, as shown by Foerster, who has also determined the velocity of the change $\text{ClO}' + 2\text{HOCl} = \text{ClO}_3' + 2\text{H}' + 2\text{Cl}'$ (see Abstr., 1901, ii, 309). The author also has determined the velocity k' of this change and finds $k_{70}' = 53.1$. From the values of k and k' it is possible to deduce the equilibrium constant K of the reversible reaction, $\text{ClO}_3' + 6\text{H}' + 5\text{Cl}' \rightleftharpoons 3\text{H}_2\text{O} + 3\text{Cl}_2$; the value thus obtained is $K_{70} = 0.995 \times 10^{-11}$. From the known heat effect of the reaction, the author then calculates $K_{20} = 0.54 \times 10^{-11}$. Further, it can be shown that an electrode immersed in a solution containing the ions H' , Cl' , and ClO_3' in equilibrium would assume the potential 1.434 volts against the normal hydrogen electrode (compare Luther, Abstr., 1902, ii, 641). J. C. P.

Atomic Weight of Iodine. PAUL KÖTHNER and E. AEUER (*Annalen*, 1904, **337**, 362—369. Compare Abstr., 1903, ii, 360—566, and this vol., ii, 81).—Baxter's recent determination of the atomic weight of iodine (this vol., ii, 81) is discussed. It is pointed out that Stas' erroneous result cannot be attributed to an admixture of silver nitrate in the silver iodide, since the same result was obtained with the sulphate. The suggestion that the iodine is possibly admixed with a small quantity of a new element is very doubtful. If the atomic weight of iodine is calculated from Ladenburg's results, using the new value found by Richards and Wells for chlorine, the number 126.985—126.991 ($\text{O} = 16$) is obtained. Baxter's calculation, $\text{I} = 126.964$, is incorrect. The most probable value for the atomic weight of iodine deduced from these two researches is 126.98. The mean of the 41 determinations made by Scott, Ladenburg, Baxter, and the authors is 126.97 ($\text{O} = 16$). K. J. P. O.

Polysulphides. I. FRIEDRICH W. KÜSTER and EDUARD HEBERLEIN (*Zeit. anorg. Chem.*, 1905, **43**, 53—84).—The solubility of sulphur in a solution of sodium sulphide is almost independent of the temperature between the limits of 0° and 50°, its solubility diminishing very slightly with increase of temperature. The solubility of sulphur in a solution of sodium sulphide depends greatly on the dilution of the

latter. It is greatest in a $N/16$ solution, where the constitution of the solution approximates to the formula $\text{Na}_2\text{S}_{5.24}$. There is evidence that in the solutions examined no uniform compounds are present, but that various substances are in a condition of complex equilibrium with one another. All sulphides and polysulphides undergo much hydrolysis in aqueous solution. The extent of hydrolysis diminishes regularly with increasing amount of sulphur in the solutions.

The representation of polysulphides as thio-salts of thio-oxy-acids is untenable, as also is Geuther's representation of them as sulphides of polyvalent metals. The formulæ advanced by Spring are also inadequate.

Polysulphides are salts of complex thio-acids of the type $\text{H}_2\text{S}_x\text{S}_x$, which are analogous to the complex iodides, HI, I_2 and HI, I_4 .

A. McK.

Theory of the Lead Chamber Process. GEORG LUNGE (*Zeit. angew. Chem.*, 1905, 18, 60—71).—Polemical. A reply to Raschig (this vol., ii, 23).

A. McK.

Density and Expansion of Sulphuric Acid in Aqueous Solution. J. DOMKE and W. BEIN (*Zeit. anorg. Chem.*, 1905, 43, 125—181).—The authors have investigated the relationships between concentration, density, and expansion of aqueous solutions of sulphuric acid and also the physico-chemical nature of sulphuric acid in various concentrations.

The maximum density, 1.8415 at $15^\circ/4^\circ$, was attained with a 97.25 per cent. of acid.

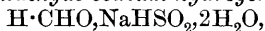
The formation of hydrates in sulphuric acid solutions is discussed. The existence of hydrates in solution cannot be deduced from density determinations alone. Examination of freezing point curves does not prove the existence of hydrates containing 1, 2, 4, and $6\text{H}_2\text{O}$ respectively.

Hydrates containing 1 and $2\text{H}_2\text{O}$ respectively certainly exist (Lespieau, Jones).

Sulphuric acid (99.52 per cent.) has a sp. gr. 1.8377 at $15^\circ/4^\circ$. The density determinations of the authors are contrasted with those of others, and extracts are given from the complete tables of the sp. gr. of aqueous solutions of sulphuric acid at various temperatures. The paper includes a very complete bibliography.

A. McK.

Constitution of Hyposulphites. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1905, [iii], 33, 129—131).—Baumann, Thesmar, and Frossard prepare *formaldehyde sodium hydrogen hyposulphite*,



by the reduction of sodium hydrogen sulphite with zinc and sulphuric acid and precipitation with sodium chloride after removal of the zinc. The precipitate is dissolved in a 40 per cent. solution of formaldehyde, when a mixture of the desired product with formaldehyde sodium hydrogen sulphite crystallises out. From this, the hyposulphite additive product may be obtained in large, monoclinic crystals by

recrystallisation from dilute alcohol. It is, like all the additive products of formaldehyde with the hyposulphites, quite stable and is only resolved into its generators by steam at 100° , and under these conditions forms a powerful reducing agent (*Rev. Gen. Mat. Col.*, 1904, 353).

The formulæ ascribed to these compounds support Schützenberger's view (*Compt. rend.*, 1869, 69, 196) that the composition of sodium hyposulphite is represented by the formula NaHSO_2 (compare Bernthsen and Bazlen, *Abstr.*, 1900, ii, 203). It is suggested that the salt $\text{K}_2\text{S}_2\text{O}_4$, obtained by Moissan by the action of sulphur dioxide on potassium hydride (*Abstr.*, 1903, ii, 75), is derived from a new sulphur acid and that it is hydrolysed by water according to the equation $\text{K}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} = \text{KHSO}_2 + \text{KHSO}_3$. In support of this view, it is stated that the product recrystallised from water contains both needles and stellate groups of acicular crystals.

T. A. H.

Colloidal Selenium. CARL PAAL and CARL KOCH (*Ber.*, 1905, 38, 526—534. Compare Schultze, *Abstr.*, 1886, 302; Gutbier, *Abstr.*, 1902, ii, 652).—The liquid hydrosol of selenium is obtained by reducing selenious acid, dissolved in aqueous sodium protalbate or lysalbate, with hydrazine hydrate and hydrochloric acid, or with hydroxylamine hydrochloride, and dissolving the precipitate so obtained in aqueous sodium carbonate. The liquid hydrosol, after purification by dialysis, is blood-red by reflected-light, or, when strongly diluted, red by transmitted light. The solid hydrosol, obtained in dark red, glistening flakes when the solution is evaporated by gentle heat and finally over sulphuric acid, contains 32—50 per cent. of selenium, and is easily soluble in cold water. This form is much more stable than the hydrosols previously obtained; in aqueous solution, it remains unchanged on repeated alternate treatment with acetic acid and sodium hydroxide, or when boiled with an excess of 10 per cent. sodium chloride or phosphate solutions, but is gelatinised on addition of an excess of calcium chloride solution in the cold. A specimen of this solid hydrosol, after preservation for $2\frac{1}{2}$ years, dissolved almost completely in water.

Colloidal selenium, containing up to 90 per cent. of selenium, is obtained by dissolving the solid hydrosol in water and adding acetic acid as long as precipitation takes place.

G. Y.

The Brown and Blue Modifications of Colloidal Tellurium. CARL PAAL and CARL KOCH (*Ber.*, 1905, 38, 534—546. Compare Gutbier, *Abstr.*, 1902, ii, 653; 1904, ii, 613).—The brown modification of colloidal tellurium is easily obtained by warming an alkaline aqueous solution of telluric acid, containing protalbic or lysalbic acid, with hydrazine hydrate on the water-bath; in neutral or alkaline solution, containing sodium protalbate or lysalbate, telluric acid is reduced by hydroxylamine only on boiling, as is tellurium dioxide by hydrazine hydrate; in these cases, the brown modification, at first formed, changes into the blue as the boiling proceeds. Gutbier and Resenschek's brownish-violet tellurium hydrosol is probably a mixture of the brown and blue modifications. As in the case of colloidal selenium, the liquid hydrosols of tellurium, containing sodium

protalbate or lysalbate, are very stable, and, on careful evaporation, yield the solid hydrosols, which are soluble in water and remain unchanged when heated to 100° in a vacuum. On addition of acetic acid to the liquid hydrosols, the solid hydrosols containing protalbic or lysalbic acid are precipitated; these contain upwards of 80 per cent. of tellurium, and are very stable when protected from the atmospheric oxygen, the brown modification retaining its solubility after three years.

G. Y.

Radiotellurium. IV. WILLY MARCKWALD (*Ber.*, 1905, 38, 591—594. Compare *Abstr.*, 1902, ii, 508; 1903, ii, 81, 733).—A quantity of crude tellurium, obtained from 15 tons of pitchblende, was treated as previously described. The product thus obtained was purified as follows. It was dissolved in dilute nitric acid and the filtered solution repeatedly evaporated with hydrochloric acid in order that the nitric acid should be expelled. A current of sulphur dioxide was then passed into the solution of the residue in dilute hydrochloric acid. The resulting precipitate consisted of a mixture of selenium, tellurium, and radiotellurium. It follows from this result that radiotellurium chloride is reducible by sulphurous acid. Radiotellurium is precipitated by sulphurous acid relatively with greater difficulty than the other substances. The precipitate (16 grams), obtained by means of sulphurous acid, was dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue warmed with ammonia, a method of separation of radiotellurium from selenium and tellurium which was based on the supposition that radiotellurium oxide is not an acid anhydride, and is quite insoluble in ammonia. Three milligrams of a very radioactive product were thus obtained.

Measurements showed that the radioactivity of this product diminished with time. The rate of decay accords with the formula for unimolecular reactions, as is the case with all uniform radioactive substances. After 139.8 days, the intensity of the radioactivity sunk to one-half of the original.

Radiotellurium is a uniform radioactive substance, and is not identical with polonium, which, without doubt, is a mixture of radioactive substances. The rate of decay of Madame Curie's polonium, as measured by her, does not accord with the formula for unimolecular reactions.

Rutherford's Radium E is also not identical with radiotellurium.

A. McK.

Formation of Ammonia from its Elements. FRITZ HABER and G. VAN OORDT (*Zeit. anorg. Chem.*, 1905, 43, 111—115).—The authors have studied the equilibrium between nitrogen, hydrogen, and ammonia. A current of ammonia was passed over finely-divided iron at a high temperature, and the resulting gas, after having been freed from ammonia, passed over a fresh quantity of iron, which was maintained at the same temperature as in the initial case. A fresh amount of ammonia was produced by the latter treatment; this was again separated from the mixture, which was now found to be a mixture of nitrogen (1 vol.) and hydrogen (3 vols.).

The experiments were conducted with dry gases at pressures approximating to atmospheric. The temperature was about 1000° . Nickel is not so active a catalyst as iron.

A. McK.

Action of Hydrogen Fluoride on Nitrogen Sulphide, and a New Method of Formation of Thionyl Fluoride. OTTO RUFF and CURT THIEL (*Ber.*, 1905, **38**, 549—553. Compare Abstr., 1904, i, 396).—When heated at 120° in a closed platinum vessel, hydrogen fluoride and nitrogen sulphide unite to form a red liquid, which easily decomposes again into its components; in presence of traces of moisture, thionyl fluoride is formed. This may be prepared almost quantitatively by heating nitrogen sulphide, hydrogen fluoride, and copper oxide together at 100° in a copper bomb.

In presence of carbon or of sunlight, a mixture of chlorine and thionyl fluoride in a sealed glass tube react with the silica of the latter to form silicon tetrafluoride and sulphuryl fluoride. Thionyl fluoride and nitrogen trioxide, in presence of traces of moisture, react with silica to form nitrosulphonic acid and silicon tetrafluoride.

Thionyl chloride is not changed when repeatedly passed through a white hot platinum tube filled with platinum sponge.

G. Y.

New Experiments on the Preparation of Diamonds. HENRI MOISSAN (*Compt. rend.*, 1905, **140**, 277—283. Compare Abstr., 1897, ii, 549).—The appearance of the cross-section of the block of meteoritic iron from Cañon Diablo (this vol., ii, 43) seemed to indicate that the separation and crystallisation of the carbon had been influenced by the sulphur, silicon, and phosphorus present in the meteorite. The author's previous experiments have therefore been repeated with a view of testing whether the presence of these metalloids affects the crystallisation of the carbon under laboratory conditions. One hundred and fifty grams of Swedish iron were melted in a crucible in the electric furnace with excess of sugar charcoal, and at the end of two or three minutes, when the molten iron had become saturated with carbon the crucible was withdrawn, five grams of ferrous sulphide were added, and the whole was then rapidly cooled by immersing the crucible in cold water. Carbon separated in crystalline form from the central portions of the molten mass, and the yield was increased as a consequence of the presence of sulphur. No diamonds were obtained on the addition of sulphide if the mass was not rapidly cooled. The presence of silicon also appears favourable to the crystallisation of the carbon, whereas experiments in which phosphide of iron was added gave no result.

The synthetical diamonds are always feebly doubly refracting, but the amount is variable and bears no relation to the external form. This observation is in agreement with the optical behaviour of most natural diamonds.

H. M. D.

Combustible Gaseous Carbon Compounds in the Air. HEINRICH WOLPERT (*Arch. Hygiene*, 1905, **52**, 151—178).—In the free outer air, there exist certain incompletely oxidised carbon compounds. The amount of these materials in the Berlin atmosphere averages at

least 0.015 volume per 1000, that is, about 4.5 per cent. of the amount of carbon dioxide. The air of rooms contains at least as much, but if this is rendered still more impure by the burning of oils or gas or by respiration, these gaseous compounds of carbon increase.

W. D. H.

The Action of Silicochloroform on some Fluorides and the Preparation and Properties of Silicofluoroform. OTTO RUFF and CURT ALBERT (*Ber.*, 1905, 38, 53—64. Compare Ruff and Plato, *Abstr.*, 1904, ii, 265).—Silicochloroform does not react with silver fluoride or lead fluoride even on prolonged heating.

Antimony trifluoride and silicochloroform react in a sealed tube according to the equation $3\text{SiHCl}_3 + 4\text{SbF}_3 = 3\text{SiF}_4 + 2\text{Sb} + 2\text{SbCl}_3 + 3\text{HCl}$. The same reaction occurs very vigorously in the case of arsenic trifluoride. Tin and titanium tetrafluorides, however, react in a different manner, for instance, $3\text{SnF}_4 + 4\text{SiHCl}_3 = 4\text{SiHF}_3 + 3\text{SnCl}_4$.

To prepare silicofluoroform, molecular quantities of silicochloroform and titanium tetrafluoride are heated together in a closed copper vessel or glass tube for 18 hours at 100—120°. The vessel is then cooled in liquid air and allowed to become warm slowly, the gases evolved being condensed by means of liquid air.

Silicofluoroform, SiHF_3 , boils at -80.2° under 758.5 mm. pressure (corr.) and melts at about -110° . It slowly decomposes in a sealed glass tube, even at the ordinary temperature, according to the equation $4\text{SiHF}_3 = 2\text{H}_2 + 3\text{SiF}_4 + \text{Si}$, the decomposition being greatly accelerated by heat. It burns in air with a very pale blue flame, the temperature of ignition being higher than that of silicochloroform: $12\text{SiHF}_3 + 6\text{O}_2 = 3\text{SiF}_4 + 3\text{SiO}_2 + 4\text{H}_2\text{SiF}_6 + 2\text{H}_2\text{SiO}_3$.

Water and sodium hydroxide decompose it thus: $2\text{SiHF}_3 + 4\text{H}_2\text{O} = \text{Si}(\text{OH})_4 + \text{H}_2\text{SiF}_6 + 2\text{H}_2$. Alcohol forms ethyl orthosilicate, $\text{Si}(\text{OEt})_4$; ether forms ethyl silico-orthoformate, $\text{SiH}(\text{OEt})_3$, and ethyl fluoride. Toluene dissolves its own volume of silicofluoroform.

The properties of the silicohalogenoform series are tabulated and compared.

C. H. D.

Silicates. V. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1905, 43, 48—52. Compare this vol., ii, 88).—The influence of the length of time during which boiling is continued in the action of calcium hydroxide solution, either alone or in presence of calcium ions, on silicic acid has been examined. The analyses quoted show that at first calcium from the hydroxide quickly combines with the silica, afterwards it is partly removed from the compound formed, and then again combined with it to a greater extent than before. The anion is in some way or other transformed.

A. McK.

Potassium and Ammonium Nitrates and the Law of Bravais. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1905, 140, 264—266).—Potassium nitrate, like ammonium nitrate, exhibits polymorphism (*Abstr.*, 1904, ii, 31), the normal orthorhombic form at 129° passing into an α -rhombohedral form, which on superfusion is converted into a β -rhombohedral variety.

M. A. W.

Some Physical Characters of the Sodium Borates, with a New and Rapid Method for the Determination of Melting Points. CHARLES H. BURGESS and ALFRED HOLT, jun. (*Proc. Roy. Soc.*, 1904, **74**, 285—295. Compare *Proc.*, 1903, 221).—When pure borax glass is kept for some hours at such a temperature that it has the consistency of a viscid syrup, it gradually changes to a mass of colourless crystals. The latter are about as soluble in water as borax glass, are not hygroscopic, and melt at a higher temperature than the glass, into which they are reconverted on melting and then cooling quickly. The phenomenon of crystallisation on reheating, moreover, is exhibited by all mixtures of boric anhydride and sodium carbonate in which the ratio $B_2O_3 : Na_2CO_3$ lies between 6 : 1 and 8 : 5. With the idea that the change was probably due to the crystallisation of some borate rich in sodium, the authors fused boric anhydride with a large excess of sodium carbonate, and found that the greatest proportion in which boric anhydride combined with sodium oxide is given approximately by $B_2O_3 : Na_2O :: 1 : 1.3$. The product obtained is therefore neither $NaBO_2$ nor Na_3BO_3 . The melting points of glasses and crystals of varying composition were determined with the view of discovering what compounds, if any, existed. A glass bead was used to attach a vertical weighted wire to a horizontal platinum wire suitably heated by a current. When the horizontal wire was raised to a sufficiently high temperature (which could be deduced from its resistance), the vertical wire dropped, and in this way the melting point of the glass was determined. The melting points of the glasses were well defined, but the melting point curve is irregular and difficult of interpretation. The melting point curve for the crystals exhibits a maximum about the composition $5Na_2O, 4B_2O_3$, which agrees with the ratio referred to above. It would appear that borax ($Na_2O, 2B_2O_3$) is not a definite compound under these conditions, but approximately a eutectic mixture of the compounds $5Na_2O, 4B_2O_3$ and $Na_2O, 4B_2O_3$, for the latter of which there is other evidence.

Experiments were also made in which, after powdering roughly, the crystals were picked out from the accompanying glass and analysed. With mixtures between $Na_2O, 4B_2O_3$ and $Na_2O, 2B_2O_3$, the crystals and the glass have the same composition, and it is probable that in this case formation of mixed crystals or a solid solution from a superfused liquid has taken place. With mixtures containing more boric anhydride than $Na_2O, 4B_2O_3$, only a part crystallises, and the crystals have approximately the composition $Na_2O, 6B_2O_3$. If the crystals could be freed from glass, the composition would probably be $Na_2O, 4B_2O_3$.

The glass must be regarded as a superfused and, therefore, metastable form of the crystals, behaving in several respects as if it were a liquid of enormous viscosity.

J. C. P.

Pentasulphides of Rubidium and Cæsium. WILHELM BILTZ and ERNST WILKE-DÖRFURT (*Ber.*, 1905, **38**, 123—130).—Rubidium and cæsium pentasulphides are formed by warming the monosulphides with powdered sulphur and aqueous alkali hydroxide solution in an atmosphere of hydrogen.

Rubidium pentasulphide, Rb_2S_5 , crystallises in dark red, rhombic prisms, commences to blacken at $170-185^\circ$, melts at $223-224^\circ$, and has a sp. gr. 2.618 at 15° . When exposed to the air, it deliquesces to a red liquid from which sulphur crystallises out; it remains unchanged under cold alcohol, hot ethyl sulphide, or chloroform, but is decomposed by hot nitrobenzene, or more energetically by a mixture of nitrobenzene with ethyl or amyl alcohols; in contact with carbon disulphide, the red crystals slowly become yellow, the change being accompanied by absorption of carbon disulphide.

Cesium pentasulphide, $\text{Cs}_2\text{S}_5 \cdot \text{H}_2\text{O}$, forms red crystals, melts at 202° , is not hygroscopic, and can be recrystallised without change from 70 per cent. alcohol. G. Y.

Some Physical Constants of Calcium and Calcium Amalgam.

HENRI MOISSAN and CHAVANNE (*Compt. rend.*, 1905, 140, 122—127. Compare Abstr., 1900, ii, 76).—The authors have redetermined some physical constants of calcium, using for the purpose the metal prepared by the Bitterfeld electrolytic process, containing from 99.3 to 99.6 per cent. of calcium, the impurities consisting of calcium chloride, silicon, aluminium, and traces of sodium and iron, and dissolving slowly in pure water, but rapidly in water containing a trace of iron, gold, or platinic chloride. The electrical conductivity of calcium, measured in wires of 0.51 and 0.77 mm. diameter, is 15.6 at 20° , that of silver being taken as 100° . Calcium becomes pasty at $790-795^\circ$ and melts at 810° (compare Arndt, this vol., ii, 87), and has a sp. gr. 1.548. Calcium dissolves slowly in mercury to form a solid crystalline mass, from which prismatic crystals of definite composition, Hg_8Ca , are isolated by fractional crystallisation in a vacuum; this amalgam is stable in dry air at the ordinary temperature, and dissolves slowly in water, thus forming a convenient reducing agent capable of reducing alkali nitrates to ammonia and traces of nitrites, ammonium sulphate to ammonium amalgam, and acetone to a mixture of pinacone and isopropyl alcohol. M. A. W.

Red Coloration of Bleaching Powder. NAZARENO TARUGI (*Gazzetta*, 1904, 34, ii, 466—468).—It is generally stated that the red coloration sometimes produced in bleaching powder by subjecting it to the action either of carbon dioxide or of gentle heat depends on the presence of small quantities of manganese which become transformed by the oxidising action of the bleaching powder into a calcium salt of permanganic acid. The author shows, however, that this is not the case, the red colour being due to the presence of a salt of ferric acid. T. H. P.

Alkaline Reaction of Strontium and Calcium Carbonates. L. BLUM (*Zeit. anal. Chem.*, 1905, 44, 12—13).—The carbonates of strontium and calcium wetted with water on red litmus paper change the colour to blue. Marble behaves in the same way. M. J. S.

Action of Barium Amalgam on Solutions of Sodium and Potassium Salts. GEORGE MCP. SMITH (*J. Physical Chem.*, 1905, 9, 13—35).—A controversial paper in which the author replies to Fernekes (this vol., ii, 33). The author's experiments show that barium in barium amalgam may be replaced by potassium or sodium by the action of solutions of the hydroxides of these metals on the amalgam. The question of such replacement is briefly discussed at the end of the paper, and it is pointed out in the case of the action of barium amalgam on solutions of potassium salts that the separation of potassium or of hydrogen depends on the relative values of the ratios $\sqrt[2]{P_{Ba}/p_{Ba}}$, P_K/p_K and P_H/p_H , where P and p are the electrolytic solution pressure and the osmotic pressure of the indicated elements. L. M. J.

Metals found in the Archeological Excavations in Egypt. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 183—185).—Two metallic specimens obtained from Egyptian tombs consist essentially of an alloy of tin and copper. The first specimen, dating from the end of the IIInd or the beginning of the IIIrd dynasty, was much corroded, and largely converted into copper oxychloride and carbonate and contained 56.7 per cent. of copper, 2 per cent. of tin, and traces of zinc. The second specimen, also from the tombs of the Pharaohs, was well preserved and contained 87.44 to 87.52 per cent. of copper, 11.47 per cent. of tin, and traces of lead. Neither specimen contained arsenic, silver, or iron. M. A. W.

Reduction of Metallic Oxides by means of the Cerite Metals. L. WEISS and O. AICHEL (*Annalen*, 1904, 337, 370—389).—The alloy of the cerite and yttrium metals, the "Mischmetall," obtained from the oxides in the residue of the manufacture of thorium nitrate, has all the requirements of a good reducing agent, as it has a high heat of combustion and forms easily fusible and stable oxides. It cannot be obtained as a powder but in filings, which, however, cannot be kept. In compact pieces, it can be kept unoxidised for months. Iron, nickel, cobalt, manganese, and chromium can easily be obtained pure by its means. Molybdenum was prepared in a pure state from molybdic acid, and forms a silver-white metal with crystalline fracture; it is not magnetic. Tungsten and uranium could not be prepared pure. Vanadium, niobium, and tantalum were easily prepared from the pentoxides. Vanadium forms a silver-white regulus, the surface of which showed crystalline structure; its hardness is 7, and it is brittle, but not magnetic, insoluble in potassium hydroxide, bromine water, hydrochloric acid, or dilute sulphuric acid, but soluble in concentrated sulphuric acid, hydrofluoric or nitric acid. It is oxidised to vanadates by molten alkali hydroxides, carbonates, or saltpetre, and when heated in the air is converted into the pentoxide. Columbium shows no sign of crystalline structure, is brittle, of a silver-white fracture, insoluble in hydrochloric or nitric acids, or aqua regia, but slowly soluble in boiling sulphuric or hydrofluoric acids. It is converted by molten alkali hydroxides into columbates, and is oxidised by the air into the pentoxide. Tantalum could not be obtained free from dross. It is

pure white and very hard, is completely insoluble in acids, but converted by alkali hydroxides into tantalates. It burns in the air to the pentoxide.

Pure metals could be obtained from the oxides of silicon, boron, tin, lead, titanium, or zirconium. Bismuth oxide reacts explosively with the alloy.
K. J. P. O.

Combinations of Samarium Chloride with Gaseous Ammonia. CAMILLE MATIGNON and R. TRANNOY (*Compt. rend.*, 1905, 140, 141—143).—When anhydrous samarium chloride (Abstr., 1902, ii, 505) is sealed in a tube with liquid ammonia, it is converted into a white, bulky compound, $\text{SmCl}_3 \cdot 11.5\text{NH}_3$, which, on being progressively heated, gives off its ammonia at eight different temperatures, which are the dissociation temperatures of the eight compounds that samarium chloride forms with ammonia; the formulæ of the compounds, their dissociation temperatures (t), and heats of formation (Q) are as follows: $\text{SmCl}_3 \cdot \text{NH}_3$, (t) 375° , (Q) 20.7 Cal.; $\text{SmCl}_3 \cdot 2\text{NH}_3$, (t) 240° , (Q) 16.4 Cal.; $\text{SmCl}_3 \cdot 3\text{NH}_3$, (t) 200° , (Q) 15.1 Cal.; $\text{SmCl}_3 \cdot 4\text{NH}_3$, (t) 155° , (Q) 13.7 Cal.; $\text{SmCl}_3 \cdot 5\text{NH}_3$, (t) 105° , (Q) 12.1 Cal.; $\text{SmCl}_3 \cdot 8\text{NH}_3$, (t) 76° , (Q) 11.2 Cal.; $\text{SmCl}_3 \cdot 9.5\text{NH}_3$, (t) 40° , (Q) 10.0 Cal.; $\text{SmCl}_3 \cdot 11.5\text{NH}_3$, (t) 15° , (Q) 9.2 Cal.
M. A. W.

Double Silicides of Aluminium. WILHELM MANCHOT and A. KIESER (*Annalen*, 1904, 337, 353—361).—A *chromium aluminium silicide*, Cr_2AlSi_3 , is obtained by heating chromium, potassium dichromate, or potassium chromifluoride with a very large excess of potassium silicofluoride and aluminium in a Perrot's furnace to the highest attainable temperature for half an hour and dissolving the regulus in dilute hydrochloric acid. It forms greyish-white, hexagonal crystals with a metallic lustre, which are conductors of electricity; their hardness is 5 and sp. gr. 4.7. It is insoluble in sodium hydroxide, boiling hydrochloric acid, nitric acid, aqua regia, or sulphuric acid, but dissolves easily in hydrofluoric acid and molten alkali hydroxides. At a high temperature, chlorine, bromine, and iodine attack the material; hydrogen chloride has a feeble action and oxygen none.

If the proportions are so chosen that the regulus contains from 34.4 to 50 per cent. of free silicon, then a second *silicide*, Cr_2AlSi_4 , is formed. It forms small crystals, of a hardness somewhat greater than 5, and a sp. gr. 4.8. It is partly dissociated at the temperature of formation. *Tungsten aluminium silicide* forms black, hexagonal crystals, which are not attacked by acids, aqua regia, or sodium hydroxide, and only by hydrofluoric acid on evaporation, but readily by hydrofluoric and nitric acids and by molten alkali hydroxides.

K. J. P. O.

Indium and Rubidium Fluorides. CAMILLE CHABRIÉ and A. BOUCHONNET (*Compt. rend.*, 1905, 140, 90—91. Compare Abstr., 1901, ii, 102, 242, 314, 600).—*Indium fluoride*, $\text{In}_2\text{F}_6 \cdot 18\text{H}_2\text{O}$, obtained by slowly evaporating a heated solution of indium hydroxide in hydrogen fluoride, forms white, crystalline needles, very slightly soluble in cold

water, insoluble in alcohol or ether, soluble in cold hydrochloric or nitric acid, and slowly decomposed by boiling with water or exposure to the air; it loses its water of crystallisation when heated, and at a red heat is completely decomposed into indium sesquioxide and hydrogen fluoride. *Rubidium hydrogen fluoride*, $\text{RbF} \cdot \text{HF}$, obtained by slowly evaporating an aqueous solution of rubidium carbonate and hydrogen fluoride, forms small, deliquescent crystals, insoluble in alcohol or ether, and partially converted into *rubidium fluoride*, RbF , when heated with excess of ammonium hydrogen fluoride.

M. A. W.

Interaction of Hydrochloric Acid and Potassium Permanganate in the Presence of Ferric Chloride. JAMES BROWN (*Amer. J. Sci.*, 1905, [iv], 19, 31—38).—Experiments have been made in which known quantities of hydrochloric acid and of standard potassium permanganate solutions have been kept at 50° for a definite time. A known volume of standard oxalic acid was then added, and standard permanganate run in until the coloration was permanent. The amounts of permanganate apparently reduced during digestion are found constant in different experiments only when the chlorine produced during the digestion is expelled by a current of air or carbon dioxide before the addition of the oxalic acid. Ferric chloride was thought by Wagner (*Abstr.*, 1899, ii, 275) to have a catalytic influence on this reaction, but the author's experiments are opposed to this view.

J. C. P.

The Increase in Volume of Molten Cast Iron saturated with Carbon in the Electric Furnace at the Moment of Solidifying. HENRI MOISSAN (*Compt. rend.*, 1905, 140, 185—192).—Pure iron, or iron containing only a small quantity of carbon, behaves normally on passing from the liquid to the solid state, that is, its volume diminishes and its density increases; iron saturated with carbon in the electric furnace behaves like water on solidifying, that is, its volume increases and its density diminishes; when, however, fused cast iron of this type is rapidly cooled by immersion in water, in fused lead, or in iron filings, a solid crust is formed, and the liquid in the interior is subjected to increased pressure due (1) to the gas evolved during the change from the liquid to the solid state, (2) to the contraction of the solid crust on cooling, (3) to the increase in volume of the interior portion on passing from the liquid to the solid state, and in these circumstances microscopic diamonds are formed in the interior of the mass due to the cooling of the fused iron saturated with carbon under increased pressure (compare *Abstr.*, 1894, ii, 189; 1896, ii, 644). If, however, as sometimes happens, the interior pressure is released by the escape of gas through a weak place in a solid crust, no diamonds are formed.

M. A. W.

A Colloidal Iron Hydroxide obtained by Electrodialysis, and some of its Properties. J. TRIBOT and H. CHRÉTIEN (*Compt. rend.*, 1905, 140, 144—146).—The colloidal ferric hydroxide obtained by dialysing a solution of ferric hydroxide on ferric chloride

always contains a considerable quantity of chlorine, which can, however, be removed by an electrolytic process, the colloidal solution containing the cathode being placed in the inner cell, the outer vessel containing water which is frequently renewed. The colloidal ferric hydroxide thus obtained possesses all the properties of Graham's hydroxide; each form behaves as a ferment towards proteid matter in alkaline medium, breaking it down into albumoses, but the colloidal ferric hydroxide, prepared as above, is more active in this respect than that of Graham, as is shown in the following table:

Colloidal Solution.	Weight of Proteid.	Alkali added.	Percentage of Albumose formed.
50 c.c. electrodialytic hydroxide	5.021	2 c.c. of $\frac{1.5\text{KOH}}{1000}$	27.02
50 c.c. „ „	5.014	2 c.c. of $\frac{1.2\text{KOH}}{1000}$	24.62
50 c.c. Graham's hydroxide ...	5.073	2 c.c. of $\frac{1.5\text{KOH}}{1000}$	8.16
50 c.c. „ „ ...	5.041	2 c.c. of $\frac{1.2\text{KOH}}{1000}$	6.23

M. A. W.

Colloidal Ferric Oxide, Brown Modification. PAUL NICOLARDOT (*Compt. rend.*, 1905, 140, 310—312).—The fact that the majority of the crystallised ferric salts are white, leads the author to conclude that the normal sesquioxide should also exhibit this colour. It is, in fact, obtained in this condition when a freshly prepared and concentrated ferric solution is added to a cooled solution of ammonia, but it rapidly becomes coloured. To explain the differently coloured forms of the oxide, it is suggested that the normal colourless oxide undergoes molecular condensation. According to the author's statements, four such modifications can be recognised.

H. M. D.

Ferrous and Ferric Arsenates. WILLIAM DUNCAN (*Pharm. J.*, 1905, [iv], 20, 71—72).—Ferrous arsenate, prepared by the B.P. method, gradually undergoes oxidation. This change is due to the action of moisture, air, and heat, which results in the formation of ferric arsenate and oxide.

Ferric arsenate, when freshly precipitated, is a dull white, insoluble substance, which becomes grey when dried at 100°, and if heated above this temperature gradually turns red. The air-dried salt has the composition $\text{FeAsO}_4 \cdot \text{H}_2\text{O}$, but becomes anhydrous if heated at 100°. When either the hydrated or anhydrous salt is treated with sodium hydrogen carbonate, effervescence takes place and a soluble compound is produced. Hydrated ferric arsenate is therefore an acid, and determinations of its basicity have shown that it may be represented by the formula $\text{AsO}_2(\text{FeO})(\text{OH})_2$.

A. ferrous ammonium arsenate has been prepared, but its stability has not yet been investigated.

E. G.

Reduction of Molybdenum Compounds in Sulphuric Acid Solution by Magnesium. BORIS GLASMAN (Ber., 1905, 38, 604—605).—Molybdic acid in sulphuric or hydrochloric acid solution, is quantitatively reduced by magnesium to molybdenum trioxide.

A. McK.

Physico-chemical Researches on Tin. VI. ERNST COHEN and E. GOLDSCHMIDT (*Zeit. physikal. Chem.*, 1904, 50, 225—237. Compare Abstr., 1904, ii, 567).—Besides grey tin, the following modifications are mentioned in older chemical literature: (1) rhombic tin; (2) tetragonal tin; (3) recently fused tin.

Special determinations of the specific gravity show that no difference can be detected between tin prepared electrolytically and tin obtained in the usual way from the fused metal. In both cases, the tin crystallises in the tetragonal form. The specific gravity of recently fused tin is 7.287 at 15°, and it appears that the very low and irregular values obtained by earlier observers for the specific gravity of electrolytic tin were due to the enclosure of varying quantities of impurity such as stannous chloride. At the ordinary temperature, rhombic tin appears to be metastable, the transition temperature lying about 170°. No indication of this is given by a dilatometer, but there is a marked change in the rate of flow of compressed tin about that temperature (compare *Ann. Physik*, 1903, [iv], 10, 647). The various stable forms of tin and the temperature limits of their stability are indicated as follows:

Grey tin $\xrightleftharpoons{20^\circ}$ tetragonal tin.

Tetragonal tin $\xrightleftharpoons{170^\circ}$ rhombic tin.

Rhombic tin $\xrightleftharpoons{232^\circ}$ fused tin.

J. C. P.

Electrolytic Recovery of Tin. F. GELSTHARP (*Trans. Faraday Soc.*, 1905, 1, 111—112).—When tin plates immersed in a solution of sodium hydroxide of sp. gr. 1.05 and at 80° were connected up with a battery, polarisation set in, and the anode surface was found to be covered with a layer of some brown substance. On reversing the direction of the current for a moment and again connecting up in the original manner, the polarisation disappeared and the tin dissolved regularly from the anode. The same effect was obtained by placing a piece of clean iron in contact with the anode for a short time.

Investigation of various pieces of tin plate showed that the phenomenon was exhibited by all bright clean samples, but not by old and tarnished (oxidised) pieces. The brown layer formed on the anode is supposed to be an oxide insoluble in sodium hydroxide solution; the effect of reversing the current or making contact with iron is to reduce this to finely divided metal, which, under the influence of the current, oxidises to form a soluble oxide. H. M. D.

Tempering of Bronzes. LÉON GUILLET (*Compt. rend.*, 1905, 140, 307—310).—Copper tin alloys, containing 5—21 per cent. of tin, have been tempered at temperatures varying from 300—800°, and the effect of the treatment on the mechanical properties determined. The

breaking weight and the elongation are slightly increased in the case of alloys containing more than 92 per cent. of copper by tempering at 400—600°. For alloys containing less than 92 per cent. of copper, these properties increase very distinctly when the temperature employed reaches 500°. This behaviour agrees with the facts brought forward by Heycock and Neville (Abstr., 1901, ii, 508; 1902, ii, 261). The maximum breaking weight is reached by tempering at 600°; the temperature which gives the maximum elongation varies with the composition of the alloy, being 800° for a bronze containing 91 per cent. copper, and 600° for one containing 79 per cent. H. M. D.

Copper, Tin, and Oxygen. E. HEYN and O. BAUER (*Chem. Centr.*, 1905, i, 76—77; from *Mitt. Tech. Vers.-A. Berlin*, 1904, 22, 137—147).—The investigations of Heyn (compare Abstr., 1904, ii, 406) on the equilibrium between copper and oxygen have been extended to the system copper, tin, and oxygen. Oxygen is only met with in copper tin alloys in the form of tin dioxide crystals, which are insoluble in the alloy. Occasionally the crystals unite to form pellicles, and as solidification proceeds the dioxide accumulates in the melted portion of the system, increasing its viscosity considerably. The tin dioxide pellicles resemble those of alumina in molten iron deoxidised by aluminium.

Cuprous oxide and tin cannot exist together in the molten alloy, reaction taking place according to the equation $2\text{Cu}_2\text{O} + \text{Sn} = 4\text{Cu} + \text{SnO}_2$. Addition of phosphorus is recommended for the removal of tin dioxide. For the analytical separation of the metallic tin from the dioxide, the alloy is made the anode in dilute sulphuric acid, when the tin present as metal passes into solution. Tin dioxide is insoluble in liquid tin. The grey and yellow spots observable on tin bronze fractures are due to the coarse structure consequent on slow cooling; if cooled rapidly, the colour of the fracture is quite uniform in consequence of the very intimate mixing of the particles. H. M. D.

Electrolytic Preparation of Titanous Sulphate. W. H. EVANS (*Mem. Manchester Phil. Soc.*, 1905, 49, Mem. II, 1—3. Compare Abstr., 1904, ii, 412).—The effect of current density, concentration of solution and temperature on the electrolytic reduction of titanous sulphate was examined. Good yields of titanous sulphate could be obtained without the use of a diaphragm. If the current density at the anode is kept fairly high, oxygen is evolved without effecting any marked oxidation of the titanous salt. The yield diminishes rapidly with increase of current density. Rise of temperature increases the yield. A. McK.

Condition in which Chlorine exists in Colloidal Solutions of Metallic Hydroxides. RUDOLF RUER (*Zeit. anorg. Chem.*, 1905, 43, 85—93).—Colloidal solutions of zirconium hydroxide, prepared by dialysis of a 3 per cent. aqueous solution of zirconium oxychloride, contain chlorine. When silver nitrate is added to such solutions, only a faint opalescence appears, the solution becoming

gelatinous after a few minutes. When nitric acid is added along with silver nitrate, a slight turbidity appears, which becomes more marked when the solution is boiled, until finally all the silver is deposited as chloride. From this and from the analogous behaviour of ferric hydroxide, the conclusion is drawn that the colloidal solutions in question contained chlorine in the form of hydrochloric acid or metallic chloride or oxychloride, dissociation having occurred partially. The behaviour of the solutions towards silver nitrate is attributed to a specific action of the colloidal hydroxide by which the silver chloride formed is retained in solution in the colloidal form. The author's views are opposed to those of Hantzsch and Desch (*Abstr.*, 1902, i, 708), who suppose that solutions of colloidal ferric hydroxychloride contain a complex chloro-ferric acid.

A. McK.

Radioactivity of Thorium. FRITZ ZERBAN (*Ber.*, 1905, 38, 557—559. Compare *Abstr.*, 1903, ii, 532; 1904, ii, 41; Wiukler, *Abstr.*, 1904, ii, 462).—Uranium has been found in all monazite sands which have been specially examined for that element. To ascertain if the monazite itself contains uranium, a well-crystallised Norwegian monazite was examined and found to contain uranium, and it yielded radioactive thorium. Minerals free from uranium yield inactive thorium (compare Baskerville and Zerban, this vol., ii, 95). G. Y.

The Spitting of Alkali Vanadates. WILHELM PRANDTL (*Ber.*, 1905, 38, 657—662).—When a mixture of vanadium pentoxide and sodium carbonate along with a small quantity of phosphoric acid is melted in the blow-pipe flame and allowed to cool slowly, a marked evolution of oxygen takes place, the whole mass spitting violently, much as solidifying silver does. *Sodium hypovanadovanadate*, $5V_2O_5 \cdot V_2O_4 \cdot Na_2O$, is formed, crystallising in dark steel-blue, glistening, rhombic needles quite insoluble in water; *potassium hypovanadovanadate*, $8V_2O_5 \cdot V_2O_4 \cdot K_2O$, has similar properties. This is an interesting case of dissociation of a compound rich in oxygen into oxygen and a substance containing less oxygen as the temperature falls.

E. F. A.

So-called Explosive Antimony. II. ERNST COHEN, EDWARD COLLINS, and TH. STRENGERS (*Zeit. physikal. Chem.*, 1904, 50, 291—308. Compare *Abstr.*, 1904, ii, 345).—According to earlier work of Pfeifer and Popper, the quantities of metallic antimony deposited by a current from solutions of the trichloride are always proportional to the quantities of silver deposited by the same current; it was found also that this ratio was independent of the concentration of the antimony trichloride solution and of the varying quantities of the trichloride enclosed in the antimony deposit.

The authors show that the influence of varying temperature and of varying hydrochloric acid concentration on the electro-chemical equivalent found for antimony is practically negligible. Their experiments show, however, that the ratio $Sb:Ag$ does increase with the concentration of the trichloride in the solution which is electrolysed; thus, as the said concentration rises from 2.3 to 83.3 per cent.

the antimony equivalent increases from 40.29 to 40.63. A similar increase of the equivalent was found with solutions of antimony trichloride in methyl alcohol, and of the tribromide and trifluoride in water. It is noteworthy that in the last case the antimony deposited is not explosive, nor does it enclose any appreciable quantity of the trifluoride. On the other hand, all the samples of antimony obtained by electrolysing the tribromide solutions (4.3—68.4 per cent. concentration) were explosive, and were found to contain large quantities of tribromide.

J. C. P.

Alloys of Zinc and Antimony. K. MÖNKEMEYER (*Zeit. anorg. Chem.*, 1905, 43, 182—196).—Since many of the results quoted in the literature concerning the compounds formed by melting together zinc and antimony are discordant, the author has studied the curve of cooling of mixtures of these metals.

The temperatures were measured by a thermo-element, the wires of which consisted of platinum and an alloy of platinum with rhodium and were connected by means of copper wires with a voltmeter. The temperatures were read every 10 seconds. Zinc melts at 410° and antimony at 630.6°.

From one series of experiments, the following are recorded: the composition of the molten mixture, the temperature at which crystallisation began (corresponding with the breaks in the curves of cooling), and the temperatures of the eutectic crystallisation (the simultaneous separation of two crystalline forms). The number of seconds is also noted during which each eutectic crystallisation lasted. The curve shows two maxima, three eutectic points, and the two melting points of the pure metals. The evidence for the existence of the compound Zn_3Sb_2 is as follows. The curve exhibits a distinct maximum corresponding with 45 per cent. of zinc. At 561°, the temperature corresponding with this maximum, the solid which separates is uniform. The crystallisation of the fused masses, containing 50 and 40 per cent. of zinc respectively, ends at 411° and 539° respectively. The presence of the compound Zn_3Sb_2 is also deduced from the structure of the alloys, containing from 40 to 50 per cent. of zinc.

The evidence for the existence of the compound ZnSb is as follows. The curve exhibits a maximum, corresponding with 35 per cent. of zinc, whilst at 544°, the temperature corresponding with this maximum, the solid which separates is uniform. The crystallisation of the fused masses containing 40 and 30 per cent. of zinc respectively ends at 539° and 507° respectively. The structure of the alloys is also evidence for the existence of this compound.

A. McK.

Gold Hydrosols. LUDWIG VANINO (*Ber.*, 1905, 38, 463—466. Compare Abstr., 1904, ii, 808).—Gold hydrosols may be prepared by warming alcoholic solutions of gold chloride with water. Sodium aurichloride is not reduced so readily. Hydrosols with different characteristic colours may be obtained by working under varying conditions of temperature and concentration. Methyl alcohol may be

used in place of ethyl alcohol, and the reaction may be carried out at the ordinary temperature, but proceeds very slowly under these conditions.

J. J. S.

Supposed Solubility of Aurous Oxide in Water. LUDWIG VANINO (*Ber.*, 1905, **38**, 462—463).—The so-called solution of aurous oxide in water is in reality a colloidal suspension, as the oxide may be precipitated together with barium sulphate or silicic acid (Vanino and Hartl, *Abstr.*, 1904, ii, 808), and cannot pass through a Puckall filter. It may also be recognised as a suspension by means of gum arabic (Muthmann, *Abstr.*, 1887, 636).

J. J. S.

Comparative Absorption of Hydrogen by Rhodium and Palladium. L. QUENESSEN (*Bull. Soc. chim.*, 1905, [iii], **33**, 191—193).—The author finds that Wilm's statements (*Abstr.*, 1881, 514), (1) that rhodium absorbs hydrogen more readily than palladium, (2) that the absorption capacity of rhodium for hydrogen varies with the method of preparation of the metal, and (3) that rhodium exhibits an affinity for hydrogen, are inaccurate.

Rhodium heated in a current of hydrogen absorbs a little of the gas, and, on exposure to air, the metal so treated gives rise to a small quantity of moisture, but no moisture is produced if, before the air is admitted, a current of dry cold carbon dioxide is passed over rhodium which has been heated in hydrogen. Further, rhodium previously heated in hydrogen evolves none of this gas when subsequently heated under reduced pressure. Palladium which has been heated in hydrogen and subsequently exposed to a current of cold dry carbon dioxide still retains the property of forming moisture when brought into contact with air.

T. A. H.

Mineralogical Chemistry.

Gases Dissolved in Minerals. K. HÜTTNER (*Zeit. anorg. Chem.*, 1905, 43, 8—13).—The gases evolved on heating separately a large number of different minerals in a porcelain tube at 800—850° in an atmosphere of carbon dioxide were collected in a Schiff's nitrometer containing a 50 per cent. solution of potassium hydroxide and analysed. The percentages of oxygen, carbon monoxide, hydrogen, and nitrogen respectively in the various mixtures are tabulated. The rare gases obtained in certain cases were not further investigated. The carbon monoxide found was not formed, as Gautier supposes, by the reduction of carbon dioxide by ferrous compounds, but by the reduction of carbon dioxide by hydrogen, nor was it present in solution in the original minerals. The hydrogen found was probably also not present in the original minerals.

Hydrogen and carbon monoxide are formed when minerals which contain water are heated in a current of carbon dioxide. Hydrogen is produced by the action of reducing agents, such as ferrous and manganoous compounds, on water vapour.

A. McK.

[Graphite from Moravia. Nigrine (?) from Bohemia.]
FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1904, 39, 399; from *Zeit. chem. Ind. Prag.*, 1902, 6 pp.).—Graphite from Tresné, in Moravia: I, light grey, scaly; II, dark grey, finely scaly; III, blackish-grey, compact.

	C.	Ash.	Water (at 150°).	Water (comb.).	Total.
I.	58.07	38.45	1.08	2.40	100.00
II.	49.04	46.33	1.96	2.67	100.00
III.	33.63	62.40	1.77	2.20	100.00

Nigrine (?) occurring in orthoclase at Polanka, near Chrudim, in Bohemia, gave:

TiO ₂ .	SiO ₂ .	Fe ₂ O ₃ .	FeO.	MgO.	Total.	Sp. gr.
70.05	0.76	28.30	0.62	0.12	99.86	4.48

L. J. S.

Composition of Fiedlerite. AUGUST B. DE SCHULTEN (*Compt. rend.*, 1905, 140, 315—316).—The mineral fiedlerite, found in 1887 as crystals in the ancient lead slags of Laurion, in Greece, has not hitherto been analysed. Analysis of colourless crystals gave the following results:

PbO.	Pb.	Cl.	H ₂ O.	Total.	Sp. gr.
29.02	51.01	17.48	2.33	99.84	5.88

The formula $\text{PbO}, 2\text{PbCl}_2, \text{H}_2\text{O}$ shows the relation of fiedlerite to laurionite ($\text{PbO}, \text{PbCl}_2, \text{H}_2\text{O}$) and penfieldite ($\text{PbO}, 2\text{PbCl}_2$), which are associated minerals in the Laurion slags.

Fiedlerite, when heated, decrepitates, becomes opaque, and loses its water at 150°. It is readily attacked by cold water, the transparent crystals soon becoming opaque.

L. J. S.

Salts from the Region of Lake Chad. H. COURTET (*Compt. rend.*, 1905, 140, 316—318).—The African desert in the neighbourhood of Lake Chad abounds in surface efflorescences of alkali salts. The salts noticed are thenardite (Na_2SO_4), sodium chloride, and trona ($3\text{Na}_2\text{O}, 4\text{CO}_2, 5\text{H}_2\text{O}$).

L. J. S.

New Mineral from the Asbestos Mines of the Lanterna Valley. LUIGI BRUGNATELLI (*Chem. Centr.*, 1904, ii, 1754; from *Rend. R. Inst. Lombardo Sci. Lett.*, 35, 869—874).—The new mineral has been found accompanying a form of peridotite, closely approximating to dunitite. It occurs in the form of aggregates of small prisms imbedded in the latter, or of a white, earthy substance covering the asbestos mineral. Analysis gave:

MgO.	CO ₂ .	H ₂ O.
41.34	22.37	36.29

corresponding with the formula $\text{MgCO}_3, \text{Mg}(\text{OH})_2, 3\text{H}_2\text{O}$; sp. gr. at 16° 2.028, hardness 2—3; it appears to be monoclinic. The name *artinite* has been given to it.

H. M. D.

Triplite from a New Swedish Locality. IVAR NORDENSKJÖLD (*Zeit. Kryst. Min.*, 1904, 39, 390; from *Geol. För. Förh., Stockholm*, 1902, 24, 412—414).—Triplite occurs in the quartz of a pegmatite-vein which is worked for felspar near the lake Lilla Elgsjön, in the parish Krokek, Government of Linköping. It is brown in colour and has the usual characters of triplite; analysis gave:

P_2O_5 .	F.	MnO.	FeO.	Fe_2O_3 .	MgO.	CaO.	Al_2O_3 .
32.05	8.72	35.23	18.43	2.38	4.46	2.10	0.37
	Na_2O .	SiO_2 .	H_2O .	Total (less O for F).			
	0.31	0.18	0.10	100.66			

L. J. S.

Artificial Production of Hopeite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1904, 27, 100—103).—Small crystals of hopeite ($\text{Zn}_3\text{P}_2\text{O}_8, 4\text{H}_2\text{O}$) are obtained by mixing solutions of zinc sulphate and disodium hydrogen phosphate, and by other methods. Larger crystals, suitable for the determination of the crystallographic and optical constants, were obtained by the following method: zinc phosphate, precipitated from solutions of zinc sulphate (45 grams $\text{ZnSO}_4, 7\text{H}_2\text{O}$ in 0.5 litre) and disodium hydrogen phosphate (37 grams $\text{HNa}_2\text{PO}_4, 12\text{H}_2\text{O}$ in 0.5 litre), is dissolved in a slight excess of sulphuric acid, the solution heated on a water-bath, and ammonia solution (3:100) added drop by drop; at the end of eight days, brilliant and limpid crystals, 4.4 mm. in length, were formed. The crystals are orthorhombic and have the characters of the natural mineral; sp. gr. 3.109.

L. J. S.

Artificial Production of Barium- and Strontium-haidingerite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1904, 27, 104—109).—Crystals of the compounds $\text{HBaAsO}_4, \text{H}_2\text{O}$ and $\text{HSrAsO}_4, \text{H}_2\text{O}$ were obtained by a method similar to that described in the preceding abstract. The crystals of both are orthorhombic and isomorphous with the mineral haidingerite ($\text{HCaAsO}_4, \text{H}_2\text{O}$) (compare Abstr., 1904, ii, 492).

L. J. S.

Artificial Production of Barium-, Lead-, and Strontium-monetite, and of Arsenated Monetites. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1904, 27, 109—123).—By the methods described in the preceding abstracts, crystals of the following compounds, isomorphous with the triclinic monetite (HCaPO_4), were obtained, each of which is described crystallographically: HBaPO_4 (orthorhombic), HPbPO_4 (monoclinic), HSrPO_4 (orthorhombic), HSrAsO_4 (triclinic), and HPbAsO_4 (monoclinic).

L. J. S.

Artificial Production of Hureaulite and Cadmium-hureaulite. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1904, 27, 123—129).—Monoclinic crystals of hureaulite ($\text{H}_2\text{Mn}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$) and of the corresponding cadmium compound were obtained by the method described in the preceding abstracts. L. J. S.

Artificial Production by a Wet Method of Anhydrous Chromates of Barium, Lead, and Strontium. AUGUST B. DE SCHULTEN (*Bull. Soc. franç. Min.*, 1904, 27, 129—137).—Crystals, 1·2 mm. in length, of crocoite (PbCrO_4) were obtained by adding a solution of potassium dichromate drop by drop to a warm solution of lead nitrate with concentrated nitric acid. Crystals of barium chromate (BaCrO_4), which are orthorhombic and isomorphous with barytes, were obtained in a similar manner. Strontium chromate, being more soluble than the corresponding lead and barium chromates, is more difficult to obtain in measurable crystals, which are monoclinic and isomorphous with crocoite; the following method was successful: ammonia was added drop by drop for a period of thirty days to a warm solution of strontium nitrate and potassium dichromate.

L. J. S.

Formation of Oceanic Salt Deposits. XXXIX. Temperatures of Transformation below 25°. JACOBUS H. VAN'T HOFF and WILHELM MEYERHOFFER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1418—1421. Compare Abstr., 1904, ii, 492).—The temperature at which Glauber's salt is transformed into thenardite is normally 32·4°, but in presence of other salts the temperature is lower. Thus in presence of sodium chloride the transformation occurs at 17·9°, in presence of sodium chloride + glaserite at 16·3°, in presence of sodium chloride + blödite at 15·3°, in presence of sodium chloride + glaserite + blödite at 13·7°. Other components besides thenardite that disappear as the temperature falls are magnesium sulphate hexahydrate at 13°, kieserite at 18°, leonite at 18°, and blödite at 4·5°.

J. C. P.

Origin of Sodalite in Syenites. STANISLAUS J. THUGUTT (*Centr. Min.*, 1905, 86—89).—The sodalite of sodalite-syenites has been considered by some authors to be of primary, and by others of secondary origin. It is pointed out that both sodalite and ultramarine (which is proved to be present in both blue and white sodalite) have been artificially prepared only by fusion, and that various attempts to obtain them by a wet method have been unsuccessful; further, sodalite is readily decomposed by water and aqueous solutions (Abstr., 1895, ii, 358). These facts are taken to prove that sodalite is always an original mineral of igneous origin. L. J. S.

[**Meerschaum and Jarosite.**] FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1904, 39, 400; from *Progr. d. čechosl. Handels. akad. Prag.*, 1903, 13 pp.).—A finely fibrous to compact, pale yellow mineral, occurring in crevices in a felspar-hornblende-rock in western Moravia,

was shown on analysis to have the composition of meerschäum
($\text{H}_4\text{Mg}_2\text{Si}_3\text{O}_{10}$) :

SiO_2 .	MgO .	CaO .	MnO .	Al_2O_3 .	Fe_2O_3 .	H_2O (comb.)*	CO_2 .	Total.
57.77	25.03	0.87	0.64	2.74	1.24	11.74	trace	100.00

* 8.49 per cent. of hygroscopic water deducted.

Jarosite, as an ochre-yellow encrustation on hæmatite from Sichotín, in Moravia, gave :

Fe_2O_3 .	Al_2O_3 .	CaO .	K_2O .	Na_2O .	SO_3 .	H_2O .	Insol.	Total.
51.05	0.40	0.46	7.50	0.28	29.40	10.88	10.88	100.57

L. J. S.

Titanolivine from Val Malenco, Lombardy. LUIGI BRUGNATELLI (*Zeit. Kryst. Min.*, 1904, **39**, 209—219).—Nodules and veins of titanolivine occur with olivine, antigorite, magnetite, &c., in the serpentine-schists at several spots in the neighbourhood of Chiesa. It is a deep cherry-red in colour and resembles garnet in appearance ; sp. gr. 3.20—3.26. The optical characters of the material point to monoclinic symmetry, as previously suggested for the mineral by Lacroix. It is sometimes twinned, and is frequently regularly intergrown with olivine. The mineral offers more resistance to weathering than does the associated olivine, but the products of decomposition, namely, antigorite and a colourless diopside, are the same for both. Analysis by G. Anelli gave :

SiO_2 .	TiO_2 .	MgO .	FeO .	MnO .	Fe_2O_3 .	F.	H_2O .	Total.
36.86	4.78	45.50	10.05	trace	1.08	trace	1.57	99.84

The ratios $(\text{Si,Ti})\text{O}_2 : \text{R}''\text{O} : \text{H}_2\text{O} = 1.06 : 2 : 0.14$ are almost identical with those obtained by Damour for the mineral from the Tyrol and Switzerland. Water is given off only at a high temperature. Titanolivine thus appears to be a distinct mineral species, and to be related to olivine as clinohumite is to humite.

L. J. S.

[**Hornblende from Bohemia.**] By HEINRICH L. BARVÍŘ (*Zeit. Kryst. Min.*, 1904, **39**, 398 ; from *Abh. böhm. Akad.*, 1902, No. 22).—In a paper on the chemical relations of some rocks from Eule, the following analysis is given of a hornblende, which was isolated from the granite of Žampach, near Eule :

SiO_2 .	TiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	CaO .
44.16	trace	8.54	8.17	14.23	0.48	10.05
		H_2O (hygros.).	H_2O (ignition).	Total.	Sp. gr.	
		10.39	1.59	99.51	3.19	

L. J. S.

[**Chrysocolla from Western Australia.**] EDWARD S. SIMPSON (*Rep. Dep. Mines, W. Austr.*, for 1903, 1904, p. 143).—A supposed occurrence of turquoise with copper and gold ores has been reported

from the Murchison district. Although of a brilliant colour like turquoise, the mineral is shown by the following analysis to be chrysocolla, and not turquoise :

SiO ₂ .	CuO.	FeO.	MgO.	Al ₂ O ₃ .	P ₂ O ₅ .	H ₂ O at 100°.	H ₂ O (ig- nition).	Total.
39.90	43.36	0.65	trace	nil	nil	9.36	7.42	100.69

The report includes various other mineralogical notes, and analyses of gypsum, diatomite, clay, and chalk. L. J. S.

[Alteration Product of Topaz.] A. KREJČÍ (*Zeit. Kryst. Min.*, 1904, 39, 399; from *Sitz.-ber. k. böhm. Ges. Wiss.*, 1902, No. xxxv, 7 pp.).—The minerals beryl, tourmaline, andalusite, and topaz from Písek, in Bohemia, are described. The alteration product of the topaz is proved by the following analysis, by F. Kovář, to be compact muscovite.

SiO ₂ .	F.	Fe ₂ O ₃ .	Al ₂ O ₃ .	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.	Sp. gr.
47.71	0.17	2.87	33.61	1.10	trace	1.04	8.12	0.84	5.11	100.57	2.45

L. J. S.

[Naëgite, a New Mineral.] TSUNASHIRŌ WADA (*Minerals of Japan, Tōkyō*, 1904).—This book contains a description of all the mineral species found in Japan, with notes on their modes of occurrence and localities, and is an extension of the paper by K. Jimbō (*Abstr.*, 1900, ii, 87). Numerous analyses which have hitherto not appeared in a European language, are quoted, and a new species, *naëgite*, is described.

The new mineral is found with fergusonite in the alluvial tin washings at Naëgi, near Takayama, in the province Mino, as green to brown spheroidal aggregates with indistinct crystals on the surface. The crystals are tabular or prismatic in habit, and appear to be tetragonal with the pyramid angle (111): ($\bar{1}\bar{1}1$) about $56\frac{1}{2}^\circ$, which is near that of zircon. Under the microscope, the mineral is grass-green and transparent, and is sometimes optically birefringent, but more often isotropic. Hardness $7\frac{1}{2}$; sp. gr. 4.09. It is pronouncedly radioactive. Analysis by T. Tamura gave :

SiO ₂ .	UO ₂ .	ThO ₂ .	Ta ₂ O ₅ .	Nb ₂ O ₅ .	CeO ₂ .	Fe ₂ O ₃ .	CaO.	MgO.	H ₂ O.	Total.
34.89	28.27	16.50	7.00	4.10	1.59	1.60	1.71	0.57	3.12	99.35

The mineral is thus mainly a silicate of uranium and thorium, and is considered to be isomorphous with zircon and thorite [but it is to be noted that the composition deviates very considerably from that of an orthosilicate]. L. J. S.

Beckelite, a Calcium Cero-lanthano-didymo-silicate. JÓZEF MOROZEWICZ (*Bull. Acad. Sci. Cracovie*, 1905, année 1904, 485—492).—The new mineral occurs as an accessory constituent of a dyke-rock composed of nephelite, albite, ægirite and magnetite, which is associated with the mariupolite (*Abstr.*, 1902, ii, 668) and elæolite-syenites of the Mariupol district on the Sea of Azov, Russia. The wax-yellow grains

and octahedral or rhombic-dodecahedral crystals, which measure up to $\frac{1}{2}$ cm. across, resemble pyrochlore in general appearance and physical characters, but have a cubic instead of an octahedral cleavage. Sp. gr. 4.15; hardness 5. The mineral is readily decomposed by acids with separation of silica. Chemically, it is quite distinct from pyrochlore, containing no niobium, titanium, or fluorine. Analysis gave:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	ZrO ₂ .	Y ₂ O ₃ , Er ₂ O ₃ .	Ce ₂ O ₃ .	La ₂ O ₃ .	Di ₂ O ₃ .
17.13	0.30	trace	2.50	2.80	28.10	13.60	18.00
Mn ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.	
0.07	15.46	trace	0.39	0.78	0.99	100.13	

The formula is $\text{Ca}_3(\text{Ce}, \text{La}, \text{Di}, \text{Y})_4(\text{Si}, \text{Zr})_3\text{O}_{15}$, which, written as $\text{Ca}_3\text{R}_2\text{Si}_3\text{O}_{12}, \text{R}_2\text{O}_3$, shows a relation to garnet, with rare earths in place of alumina, and an analogy to calcium aluminosilicate.

L. J. S.

Orbicular Gabbro from California. ANDREW C. LAWSON (*Bull. Dept. Geol. Univ. California*, 1904, 3, 383—396).—A petrological description is given of the various facies of an outcrop of gabbro at Dehesa, San Diego Co. The normal type is a coarse-grained hornblende-gabbro with olivine and hypersthene. The spheroids of the orbicular type measure about 6 cm. across, and consist of a core of felspar surrounded by concentric shells of radially crystallised olivine and felspar. Analysis of the spheroids gave the results under I (by J. W. Howson), and of the felspar (anorthite) isolated from them the results under II (by W. T. Schaller):

SiO ₂ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	Total.
40.08	22.86	11.96	12.40	11.41	1.26	0.38	100.35
44.39	36.55	trace	nil	18.67	0.83	—	100.44

L. J. S.

Physiological Chemistry.

The Power of Human Blood to Decompose Hydrogen Peroxide. HERMANN SILBERGLEIT and MAX MOSSE (*Chem. Centr.*, 1905, i, 268—269; from *Beitr. klin. Med. Festschrift*, 1904).—The same amount of hydrogen peroxide is decomposed in the same time by the same amount of blood from healthy people with the normal amount of hæmoglobin and corpuscles. The catalytic power of the blood runs parallel with the number of corpuscles. W. D. H.

Peptic and Tryptic Digestion of Proteids. II. D. LAWROFF (*Zeit. physiol. Chem.*, 1905, 43, 447—463).—The prolonged action of

0.5 per cent. hydrochloric acid leads to the formation, only more slowly, of the same products as those formed during peptic digestion. The experiments were mainly performed with gelatin and hæmoglobin.
W. D. H.

Pancreas and Glycolysis. RICHARD CLAUS and GUSTAV EMBDEN (*Beitr. chem. Physiol. Path.*, 1905, **6**, 214—231. Compare Cohnheim, *Abstr.*, 1903, ii, 738; 1904, ii, 675).—Polemical, mainly against Cohnheim's view that the pancreas exercises power in promoting glycolysis in muscle. Cohnheim's results are not confirmed.

W. D. H.

Physiology of Mollusca. I. LAFAYETTE B. MENDEL and HAROLD C. BRADLEY (*Amer. J. Physiol.*, 1905, **13**, 17—29).—Digestion in *Sycotypus* is effected by the salivary glands and the hepato-pancreas. The former histologically resemble those of higher animals; their secretion contains mucin and a proteolytic enzyme which normally acts in the cold and in solutions which are neutral or amphoteric; it closely resembles trypsin. The liver or hepato-pancreas contains an amylase, invertase, and lipase. Digestion occurs in the stomach and in the hepatic ducts; absorption occurs in the same situations.

W. D. H.

Movements of the Alimentary Canal after Section of Nerves. W. B. CANNON (*Proc. Amer. Physiol. Soc.*, 1904, xxii; *Amer. J. Physiol.*, **13**).—X-Ray observations were made on the movements of the food mixed with bismuth subnitrate. After vagu ssection, there is stasis in the œsophagus, and the advance from the stomach is a little slowed, but almost normal. Stomach and intestinal movements also continue after cutting the splanchnics. The stomach movements are inhibited by distress in both conditions. The difference in the rate of discharge of carbohydrates and proteids was also preserved in both conditions.

W. D. H.

Carbohydrate Combustion in the Animal Organism. JULIUS STOKLASA (*Ber.*, 1905, **38**, 664—670. Compare Stoklasa and Czerný, *Abstr.*, 1903, ii, 320, and 1904, i, 275).—It is shown that the crude enzymes obtained from previously frozen muscles possess practically no activity as compared with the enzymes separated from the same parts when fresh and unfrozen. Special experiments were made to show that the fermentative action is not due to bacteria as suggested by Cohnheim (this vol., ii, 675). Experiments, which will be described later in detail, have shown that in the decomposition in presence of air of carbohydrates by the enzymes of muscle extract, in addition to lactic acid, alcohol, and carbon dioxide, there are formed acetic acid, a little formic acid, and hydrogen. A hypothetical scheme of the degradation of dextrose by the enzymes in question is appended.

W. A. D.

Physiological Economy in Nutrition. RUSSELL H. CHITTENDEN (published in book form, 1904, 1—478, New York).—A full account of experiments carried out on the author's own person, on that of his

colleagues and students, and on soldiers and athletes. Each experiment lasted for many months. The diet taken, the excreta, the body weight, the general health, tests of strength, and of mental sharpness are the points mainly considered. The general conclusion reached is that the proteid intake may be reduced to one-half or one-third of the usually accepted standard, not only without harm, but with great advantage; equilibrium is maintained, health improves, bodily and mental vigour increase. Modern diet is condemned as not merely uselessly excessive, but positively harmful. The importance of the question, and of the results attained, can hardly be exaggerated. W. D. H.

Gelatin as a Substitute for Proteid in Food. J. R. MURLIN (*Proc. Amer. Physiol. Soc.*, 1904, xxix—xxx; *Amer. J. Physiol.*, 13).—In dogs, it is a matter of indifference how much of the proteid-nitrogen is replaced by gelatin-nitrogen up to one-half of the starvation requirement. Even if two-thirds is replaced, equilibrium is maintained provided the carbohydrate amounts to one-half to two-thirds of the calorific requirement. Corresponding results were obtained in man.

W. D. H.

Proteid Synthesis in the Animal Body. VALDEMAR HENRIQUES and C. HANSEN (*Zeit. physiol. Chem.*, 1905, 43, 417—446).—From experiments on rats, it was found that the products of decomposition of casein formed by acids will not maintain the body in nitrogenous equilibrium, even if given in large quantities, but that if the products are obtained by means of proteolysis by trypsin and erepsin, nitrogenous equilibrium is maintained, or nitrogen may even increase. The same is true for the products of tryptic digestion, which are not precipitable by phosphotungstic acid (monoamino-acids), and for those products which are soluble in warm 96 per cent. alcohol. The products which are insoluble in alcohol do not possess this property.

W. D. H.

Influence of Carbohydrate Diet on the Composition of the Child. FRANZ STEINITZ and RICHARD WEIGERT (*Beitr. chem. Physiol. Path.*, 1905, 6, 206—213).—An opportunity arose of making analyses of four infants who had died from malnutrition, due to an excess of carbohydrate in the food. The analyses bring out a low percentage of water and salts, and a high percentage of fat.

W. D. H.

Effect of Blood on the Kidney. TORALD SOLLMANN (*Proc. Amer. Physiol. Soc.*, 1904, xxxi; *Amer. J. Physiol.*, 13).—Viscid solutions of egg-white and gum acacia markedly decrease vein and ureter flow and kidney volume. Dilute defibrinated blood produces the same effect several days after excision. If freshly excised kidneys are used, the vein-flow is increased; the dilator effect is also produced by blood saturated with carbon monoxide, by blood laked at 63°, and by serum; it is destroyed by coagulating the proteids. The effects, however, vary with different kidneys and different samples of blood. Hydro-

cyanic acid is also a dilator ; so also is adrenaline under certain conditions.
W. D. H.

Effects of Isotonic Solutions on the Kidney. TORALD SOLLMANN (*Proc. Amer. Physiol. Soc.*, 1904, xxx ; *Amer. J. Physiol.*, 13).—Excised kidneys were perfused with solutions isotonic with 1 per cent. sodium chloride solution. Cane sugar and dextrose cause very slight changes. Alcohol and urea diminish the vein and ureter flow and the kidney volume ; they penetrate the cells. In regard to cations, barium, calcium, and hydrogen produce the same effect ; magnesium increases both flows ; potassium and ammonium have little or no effect. In regard to anions, sulphate and citrate increase, and hydroxide, carbonate, and hydrogen carbonate lessen the flow. All these effects are removable by subsequent perfusion with sodium chloride. Locke's solution (*minus* the sugar) causes a slight increase of ureter flow, without changes in the venous flow or kidney volume. These effects can be produced several days after excision.
W. D. H.

Rate of Absorption from Intra-muscular Tissue. S. J. MELTZER and JOHN AUER (*Proc. Amer. Physiol. Soc.*, 1904, xxxii—xxxiii ; *Amer. J. Physiol.*, 13).—Absorption from the intra-muscular tissue is incomparably more rapid and efficient than from the subcutaneous tissue.
W. D. H.

Alcohol in Animal Organs. MAURICE NICLOUX (*Zeit. physiol. Chem.*, 1905, 43, 476. Compare Abstr., 1904, ii, 595).—Landsberg (Abstr., 1904, ii, 499) has confirmed in the main the author's previous results by his method. The present communication relates to some details in technique.
W. D. H.

Physiology of Glycogen. WERA ADAMOFF (*Zeit. Biol.*, 1905, 46, 281—301).—Chickens just out of the shell contain little or no glycogen. Four days later, the glycogen begins to increase. New-born rabbits yield 4.36 grams of sugar from glycogen per kilo. of body weight ; this amount is small compared to that in well-fed adult dogs. The human liver from later foetal periods contains glycogen, but not more than is obtainable from an adult animal in a state of inanition. Abundance of glycogen is therefore not a characteristic of embryonic tissues. The energy of growth and amount of glycogen are not related.
W. D. H.

Lactic Acids in the Animal Organism. G. MORIYA (*Zeit. physiol. Chem.*, 1905, 43, 397—401).—The statement is generally made on the authority of W. Müller (*Annalen*, 1857, 103, 152) and of Gscheidlen (*Pflüger's Archiv*, 1874, 8, 178) that the lactic acid obtained from the brain is not sarcolactic acid, but fermentation lactic acid. This, however, is incorrect ; the acid present is sarcolactic or *d*-lactic acid as in other organs. It was identified not only in the brain of several kinds of animals, but also in lymph glands, kidneys, thymus, spleen, pancreas, and thyroid.
W. D. H.

Para-lactic Acid. ARTHUR R. MANDEL (*Proc. Amer. Physiol. Soc.*, 1904, xvi; *Amer. J. Physiol.*, 13).—After producing phloridzin diabetes in a fasting dog poisoned with phosphorus, the urine reaction changes from ammoniacal to acid (Lusk). It seemed possible that lactic acid, which is produced in phosphorus poisoning, and is probably the cause of the excess of ammonia in the urine, might be derived as a cleavage product of sugar which originates from proteid. If this is so, no lactic acid should be formed in diabetes, even although phosphorus poisoning is present. This is the case; the blood and urine of a fasting dog poisoned with phosphorus contained lactic acid; this disappears when diabetes is induced by phloridzin.

Ingestion of fermentation lactic acid in diabetes leads to a slight reduction of proteid metabolism, and therefore of sugar output. A synthesis of a small quantity of lactic acid into sugar also seems to occur.

W. D. H.

Origin of Creatinine. WALDEMAR KOCH (*Proc. Amer. Physiol. Soc.*, 1904, xix; *Amer. J. Physiol.*, 13).—The relation of the methyl groups of lecithin to that of creatinine suggested feeding experiments with lecithin added to a creatine-free diet; the amount of lecithin given varied from 0.5 to 7 grams a day, but the amount of creatinine only varied slightly. Excess of lecithin is probably stored, for it does not appear in the faeces. Another factor (proteid katabolism) is involved in supplying most of the nitrogen of the creatinine molecule.

W. D. H.

The Source of Substances containing Sulphur in Animals. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1905, 43, 469—475).—Cystin is regarded as a source of the gaseous products hydrogen sulphide, methyl mercaptan, and ethyl sulphide, as it is also of taurine and of sulphates, non-oxidised sulphur, and sulphites. The seat of formation is probably the intestine.

W. D. H.

Histological Changes in Wool-fibre by the Prolonged Action of Water. Chemical Nature of the Wax of Corpses. NAZARENO TARUGI (*Gazzetta*, 1904, 34, ii, 469—474).—The author has examined the woollen sock of a drowned man who had remained under water for more than 22 months. The boot had prevented the swelling of the foot, which had taken up the shape of the boot. The total absence of any part of the sock outside the boot showed that the continuous action of the water had completely destroyed the woollen tissue by slow oxidation processes and mechanical action. The part of the sock inside the boot had been kept intact by a substance which had filtered into the wool, and which the author finds to consist mainly of palmitic acid. This acid is formed by the slow oxidation of the fatty substance of the foot.

T. H. P.

Staining Reactions of Animal Cells. MAX MOSSE (*Chem. Centr.*, 1905, i, 386; from Salkowski's *Festschrift*, 1904).—The paper mainly treats of histological methods, and especially of the different solubilities and staining reactions of nuclein and paranuclein (nucleoli).

Acid dyes are stated to colour the nuclein, and ammoniacal dyes the paranuclein, best. Absolute alcohol and then mercuric chloride are the best indifferent fixatives.

W. D. H.

Reversal of Ciliary Movement in Metazoa. G. H. PARKER (*Amer. J. Physiol.*, 1905, 13, 1—16).—The reversal of the effective stroke in the cilia of protozoa is well known. It is rarer in metazoa. The present experiments were made in the labial cilia of the anemone *Metridium marginatum*. The majority of the substances tried produce no effect. Reversal is not produced by changes in osmotic pressure, nor by anions, but by potassium-ions. The reversal observed with crab meat juice depends on organic compounds of potassium; if the extractives are removed, crab meat has no effect.

Irreversible cilia are probably not symmetrical, in that they consist of a supporting elastic element, on one side of which is contractile material.

W. D. H.

Eck's Fistula in Dogs. PHILIP B. HAWK (*Proc. Amer. Physiol. Soc.*, 1904, xiv; *Amer. J. Physiol.*, 13).—This operation was successfully performed in two dogs, who lived for 59 and 30 days respectively. The liver function was much impaired. The dogs lost greatly in body weight, and exhibited ataxy and cataleptic attacks while they lived. Feeding with sodium carbamate, or injection of this salt into the blood stream of normal dogs, did not produce these symptoms.

W. D. H.

Iron in Mother's Milk. WILLIAM CAMERER (*Zeit. Biol.*, 1905, 46, 371).—As an addition to former data, fresh analyses are given of a specimen of human milk from the third to the twelfth days of lactation. In one analysis, 100 c.c. of milk contained 21 mg. of Fe_2O_3 , and 100 grams of ash contained 66.4 mg. In a second analysis, the numbers were 0.13 and 50.2 respectively.

W. D. H.

Formation of Acids by Enzymes. J. E. HINKINS (*Amer. Chem. J.*, 1905, 33, 164—167).—A series of experiments has been made to determine the action of diastase and pancreatin on solutions of triacetyldextrose in presence of peptone. The results show that in each case the solutions gradually become acid. A study was also made of the combined effect of bacteria and enzymes on the solution. It was found that when the liquids containing diastase or pancreatin were treated with cultures of bacteria taken from the mouths of persons having severe tooth erosion and were kept at 37°, a larger amount of acid was produced than in the absence of the bacteria. It is shown that solutions rendered acid by the action of enzymes readily dissolve cements employed for tooth fillings. It is concluded that the abnormal increase in the acidity of the saliva of persons suffering from tooth erosion is probably due to the action of enzymes on certain constituents of the saliva.

E. G.

Normal Urine. OTTO FOLIN (*Amer. J. Physiol.*, 1905, 13, 45—65, 66—115).—The tables giving the composition of normal

urine in most text-books are derived from the old analyses of Parkes, and thus date from a time before the introduction of the Kjeldahl method, and before the importance of the estimation of total nitrogen was recognised. Bunge calls attention to the fact that in the voluminous literature on the urine there is still no record of the complete analysis of any one concrete sample of a normal 24 hours' urine. Hopkins points out the importance of the urinary analysis being considered in relation to the diet. The first of the present papers aims at repairing this gap in statistics, the second deals with the laws governing the composition of normal urine. Complete analyses are presented of thirty urines from six normal persons, all kept for seven days on a uniform diet; the urine in each case was analysed for the last five days only of the period. The diet contained 119 grams of proteid, 148 of fat, and 225 of carbohydrate, that is, it approximates to the old Voit standard. The estimations made were of total nitrogen, urea, ammonia, creatinine, uric acid, chlorides, phosphates, total sulphur, sulphates of both kinds, "neutral sulphur," indican, total acidity, and mineral acidity.

The final averages for the 24 hours' urine are as follows :

Volume of urine	1430 c.c.
Total nitrogen	16 grams.
Urea...	29.8 "
Urea nitrogen	13.9 "
Ammonia nitrogen	0.7 "
Creatinine	1.55 "
Creatinine nitrogen	0.58 "
Uric acid	0.37 "
Uric acid nitrogen	0.12 "
Undetermined nitrogen	0.60 "

The following are the results in percentages of total nitrogen : urea, 87.5; ammonia, 4.3; urea and ammonia, 91.8; creatinine, 3.6; uric acid, 0.8; undetermined, 3.75.

The results regarding non-nitrogenous constituents are :

Total sulphur as SO_3	3.31 grams.
Inorganic SO_3	2.92 "
Ethereal SO_3	0.22 "
"Neutral" SO_3	0.17 "
Acidity	617 c.c. of $N/10$ solution.
Mineral acidity	304 "
Organic acidity	313 "
Total phosphates...	3.87 grams P_2O_5 .
Chlorine	6.1 grams
Indican (Fehling's solution = 100)	77

The average weight of the people investigated was 63.4 kilos.

The numbers correspond very well to what has hitherto been considered normal.

The question next arises, what should be considered normal? The foregoing can only be considered normal on the basis of Voit's normal diet.

But there are races of mankind who take a very different diet, and yet are normal. There are individuals like vegetarians, and those who for various reasons have reduced their diet, particularly so far as proteid is concerned, much below the Voit standard; they remain normal, but their urine has a very different composition. The urine of one such person gave total nitrogen 4 to 8 grams; urea nitrogen, 62 to 80; ammonia nitrogen, 4.2 to 11.7; creatinine nitrogen, 5.5 to 11.1; uric acid nitrogen, 1.2 to 2.4; undetermined, 4.8 to 14.6 per cent. of total nitrogen. The wide variations were due to temporary changes in the diet, but the low urea value and the higher values of the other nitrogenous constituents would more accurately represent the usual condition on the subject's usual diet.

What is particularly noticeable in such persons is the comparatively low value of the urea nitrogen, and the first law laid down is that the distribution of the nitrogen depends on the absolute amount of total nitrogen present. There are similar differences in the distribution of the sulphur, and a similar rule is laid down. The amount of creatinine is specially interesting; on a nitrogen-rich diet, it only accounts for 3.6 per cent. of the nitrogen, whereas on a diet poor in nitrogen the urea nitrogen may sink to 62 per cent. and the creatinine nitrogen rise to 11 per cent. of the total. The absolute quantity of creatinine excreted in the same person on both diets is the same; there are individual differences between different people; corpulent people excrete less than thin people. Creatinine excretion is an index of one kind of proteid metabolism, and demands further study. Burian and Schur reached a very similar conclusion regarding endogenous purine. The conclusion drawn from the present work regarding uric acid is that the excretion of this substance in reduced proteid metabolism is diminished, but not nearly in proportion to the total nitrogen, hence the percentage of uric acid nitrogen is increased. A clear line of division between endogenous and exogenous purine, as postulated by Burian and Schur, was not wholly confirmed in the present work. With regard to ammonia, the following general conclusion is drawn: a pronounced reduction of the total nitrogen is accompanied by a relative rise in ammonia nitrogen, provided the food is not such as to yield an alkaline ash; and further, the absolute quantity of undetermined nitrogen increases under the influence of a diet poor in nitrogen, but there is a relative increase.

The only nitrogenous substance which suffers a relative as well as an absolute decrease with nitrogen-poor food is urea; the percentage of urea-nitrogen in normal human urine, as well as in nearly all pathological urine, is often reduced to 60 per cent. of the total. A further reduction is probably abnormal, although that is still unsettled.

Urinary indican is an approximate measure of intestinal putrefaction; the ethereal sulphates are not so, being only partly produced in this way; they represent a form of sulphur metabolism which becomes more prominent when the food contains but little proteid; the neutral sulphur is not at all due to processes similar to those which give rise to indican, but is in the main independent of the total sulphur and of katabolised proteid. Accurate sulphur determinations are, however, at present beset with errors of technique.

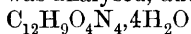
The volume of urine depends directly on the amount of water taken

in ; variations not due to variations of intake are related to the reciprocal action of the skin. Provided the chloride intake is constant, the chlorine elimination varies with the volume of the urine.

The phosphates in clear acid urine are all monobasic ; the acidity is ordinarily greater than the acidity of all the phosphates, the excess being due to free organic acids ; the mineral acidity decreases, and often is a *minus* quantity on a proteid-poor diet. The organic acids do not diminish so much.

W. D. H.

Urine of the Coyote. ROBERT E. SWAIN (*Amer. J. Physiol.*, 1905, 13, 30—34).—Kynurenic acid has hitherto been found only in dog's urine ; it is absent even in the fox and wolf. It is, however, present in the urine of the coyote, an animal closely related to the dog and inhabiting the arid districts of N.W. America. The total nitrogen is 36.4 grams per litre, most of which is present as urea. The amount of kynurenic acid is 0.4 gram per litre. A crystalline deposit found in the urine was analysed, and the formula



assigned to it. Jaffe's urocanic acid has the formula $\text{C}_{12}\text{H}_{12}\text{O}_4\text{N}_4, 4\text{H}_2\text{O}$. Further investigation of this new material is promised.

W. D. H.

Acidity of Urine. HEINRICH DRESER (*Beitr. chem. Physiol. Path.*, 1905, 6, 178—190).—What is termed the intensity of acidity is regarded as an important factor in the therapeutic action of urinary disinfectants, such as camphoric and salicylic acids. In acid human urine, the acidity obtained by titration with alkali is often twice or thrice as great as that reckoned from the amount of acid phosphate. The urinary acidity cannot therefore depend on a mixture of primary and secondary alkali phosphates.

W. D. H.

Elimination of Creatinine. LAFAYETTE B. MENDEL and OLIVER E. CLOSSON (*Proc. Amer. Physiol. Soc.*, 1904, xix—xx ; *Amer. J. Physiol.*, 13).—Data on this question are meagre and conflicting. There is a noteworthy excretion of this substance in vegetarians and those on a low proteid diet. On a creatine-free diet, there is a tendency to parallelism between total nitrogen output and the excretion of creatinine.

W. D. H.

Urea in Human Urine. WILLIAM CAMERER (*Zeit. Biol.*, 1905, 46, 322—370. Compare Abstr., 1903, ii, 688).—A critical analysis of methods and results.

W. D. H.

Bence-Jones Proteid. LUGWIG LINDEMANN (*Chem. Centr.*, 1905, i, 269—270 ; from *Arch. klin. Med.*, 81, 114—118).—A case in which this proteid occurred in the urine is described. Its characters resemble those described by others in the main. It is regarded as an albumose.

W. D. H.

Behaviour of *p*-Dimethylaminobenzaldehyde in Animal Metabolism. MAX JAFFÉ (*Zeit. physiol. Chem.*, 1905, 43, 374—396).—*p*-Dimethylaminobenzaldehyde, dissolved in hydrochloric acid, is a

reagent which gives a red colour with normal urine; this reaction is increased in certain pathological cases, mainly of abdominal disease. What substance in urine gives the colour is uncertain. If the drug itself is given to rabbits, it is excreted mainly in combination with glycuronic acid, but among other substances found also in the urine are *p*-dimethylaminobenzoic acid and *p*-methylanilobenzoic acid.

W. D. H.

Pigments originating from Scatole and the Scatoxyl Question. CH. PORCHER and CH. HERVIEUX (*J. Pharm. Chim.*, 1905, [vi], 21, 55—65. Compare Abstr., 1904, [ii], 577).—The chromogen appearing in the urine, after administration of scatole, on a milk diet, is, in the authors' opinion, a derivative of a scatoxyl, probably $C_6H_4 \begin{smallmatrix} \text{CHMe} \\ \text{NH} \end{smallmatrix} > CO$. It is not, as supposed by Maillard, indirubin.

The colour due to scatole differs from those due to indole in its insolubility in chloroform, and, further, it is withdrawn by dilute alkali from the amyl alcohol solution, being reproduced on acidification.

G. D. L.

Diabetes Mellitus. GRAHAM LUSK and ARTHUR R. MANDEL (*J. Amer. Med. Assoc.*, July, 1904; *Deut. Archiv. klin. Med.*, 1904, 81, 472—492).—A rapidly fatal case of diabetes is recorded. There was low acidosis, and a trace of albumin in the urine; on a meat diet, the dextrose : nitrogen ratio was 3.65 : 1. This is the same as in phloridzin diabetes in dogs, and was unaltered by fat digestion or fat metabolism. The sugar was derived from proteid alone. There was complete intolerance for carbohydrates; 85 per cent. of starch and 80 per cent. of lævulose given being excreted as sugar in the urine. Withdrawal of carbohydrate food had no effect on urinary nitrogen. Urea elimination was normal. The significance of the 3.65 : 1 ratio in a meat diet is very great. It indicates a rapidly fatal result.

W. D. H.

Experimental Diabetes. FRANK P. UNDERHILL (*Proc. Amer. Physiol. Soc.*, 1904, xxxvi; *Amer. J. Physiol.*, 13).—Piperidine causes diabetes and hyperglycæmia if painted on the pancreas, intraperitoneally or intravascularly injected. This substance and a number of others, including narcotics, various alkaloids, and possibly adrenaline, appear to have no particular influence on the pancreas, but probably act on the respiratory centre, producing dyspnœa and thus a diabetic condition secondarily.

W. D. H.

Soaps in Certain Pathological Conditions. OSKAR KLOTZ (*Proc. Amer. Physiol. Soc.*, 1904, xxi—xxii; *Amer. J. Physiol.*, 13).—In certain calcareous deposits, the centre is composed of calcium salts; the periphery contains potassium, sodium, and ammonium soaps. As degeneration continues, these are converted into calcium soaps, and finally into calcium phosphate and carbonate. Soaps may also be demonstrated in pus, and a calcium soap is formed during fat necrosis.

W. D. H.

Behaviour of Guanine in the Rabbit. ALFRED SCHITTENHELM and ERNST BENDIX (*Zeit. physiol. Chem.*, 1905, **43**, 365—373).—Intravenous or subcutaneous injection of guanine dissolved in sodium hydroxide leads, in rabbits, to a great increase of purine substances, especially uric acid, in the urine. W. D. H.

Action of Urotropin and Allied Compounds. ARTHUR NICOLAÏER (*Chem. Centr.*, 1905, i, 283—284; from *Arch. klin. Med.*, **81**, 181—223).—The use of urotropin and a number of similar compounds in the treatment of bacterial invasion of the urinary passages is attributed to the fact that in decomposition these substances yield formaldehyde. Urotropin methylenecitrate yields by heating much more formaldehyde than urotropin, but has no stronger effect on the urine than urotropin itself. This compound owes its therapeutic effect only to the urotropin it contains. Formaldehyde is also a solvent of uric acid. W. D. H.

Ricin. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, 1904, xxxii; *Amer. J. Physiol.*, **13**).—The castorbean proteids were fractionated by neutral salts into portions with great and slight toxicity, and ricin was prepared in a pure form. The toxic preparations sediment red corpuscles; this property is lost when the proteid is heated to coagulation point. Pure ricin can be kept for months without deterioration. After administration, toxic symptoms do not occur until after a latent period of 15 hours. The toxicity is enormously diminished if ricin is given by the alimentary canal.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Calcium Sulphate on the Decomposition of Starch and Albumin in the Mashing Process. WILHELM WINDISCH and H. BODEN (*Chem. Centr.*, 1905, i, 305; from *Woch. Brauerei*, 21, 775).—Calcium sulphate diminishes the diastatic power of malt, especially if previously weakened by high temperature or in mashing or kiln-drying, but does not act on yeast. Unfermentable decomposition products of starch are formed, but are converted into fermentable forms by *Mucor amylomyces Rouxii*, whilst with yeasts of high fermenting power such as *Schizosaccharomyces Pombe* no decrease is caused by calcium sulphate.

The nitrogen content of the wort is increased to an extent depending on the proportion of calcium sulphate and the temperature, commencing at 20° and attaining a maximum at 60°. The increase in nitrogen is about one-fifth, and is due to degradation products of albumin, particularly to amino-acids. Calcium sulphate facilitates the action of peptase, and also the coagulation of the proteids.

G. D. L.

Contribution to Cell Chemistry. VICTOR C. VAUGHAN (*Proc. Amer. Physiol. Soc.*, 1904, xi—xii; *Amer. J. Physiol.*, 13).—Bacteria are washed with dilute alcohol and extracted with alcohol and then with ether. They are powdered and heated with sodium ethoxide. This splits the cells into two portions, A and B. A constitutes about a third of the cell substance; it is freely soluble in water and in alcohol, gives the proteid reactions, and contains the intracellular toxin of the bacillus. Animals treated with it yield an antitoxic serum. B is insoluble in alcohol, and animals treated with it furnish a bacteriolytic, but not an antitoxic serum.

W. D. H.

Action of Different Lactic Ferments on Cheese-ripening. ED. VON FREUDENREICH and J. THÖNI (*Centr. Bakt. Par.*, 1905, ii, 14, 34—43).—The lactic acid bacteria have the chief rôle in cheese-ripening, but it is still uncertain which of them are the most favourable. As a rule, the best cheeses were those which contained the most decomposition products, and those which most resembled Emmenthaler cheese were found to contain *Bacillus c*, although *Bac. a* also gave good results. *Bacterium lactis acidii* seems to be necessary.

When artificial rennet alone is employed, ripening does not go on so satisfactorily. The ripening is, however, normal when suitable bacteria are employed in conjunction with artificial rennet, and it is probable that in time this method will be found to be as beneficial as in the case of butter.

N. H. J. M.

Sensitiveness of Putrefactive and Lactic Acid Bacteria towards Poisons. OTTO RAHN (*Centr. Bakt. Par.*, 1905, ii, 14, 21—25).—Putrefactive bacteria and mould fungi resist the action of poisons much more than lactic acid bacteria, except in the cases of menthol and sodium benzoate. Mercuric chloride, formalin, boric acid, and salicylic acid acted more strongly in boiled milk, whilst copper sulphate, sodium benzoate, phenol, and menthol were more active in pasteurised milk. Formalin had very little effect on mould fungi and yeast.

N. H. J. M.

Nitrogen-fixing Bacteria. HUGO FISCHER (*J. Landw.*, 1905, 53, 61—66).—Out of six soil samples from differently manured plots, only two from the plots which had received lime were found to contain *Azotobacter*. The original soil is a heavy loam, with only 0.145 per cent. of lime.

N. H. J. M.

Presence and Distribution of Nitrogen-fixing Bacteria in the Sea. KEUTNER (*Chem. Centr.*, 1905, i, 395; from *Wiss. Meeres-unterss. Abt. Kiel*, 8).—The nitrogen-fixing bacteria *Azotobacter chroococcum* and *Clostridium Pasteurianum* are widely distributed in the ocean. The former still shows the power of fixing nitrogen in an 8 per cent. solution of sodium chloride. The bacteria are found on algæ and on plankton organisms, and also occur in many fresh waters.

G. D. L.

Biochemical Mechanism of the Fermentation of Uric Acid. CELSO ULPANI and M. CINGOLANI (*Gazzetta*, 1904, **34**, ii, 377—404. Compare Abstr., 1904, ii, 138 and 139).—The authors' experiments show that the uric acid bacterium only attacks and ferments substances the molecules of which consist of a three-carbon atom chain, of which the two outer carbon atoms are in the form of carboxyl, whilst the middle carbon atom can be more or less completely oxidised. Fermentation also occurs with compounds in which this molecular grouping is combined with the carbamide nucleus, but in this case the oxidation of the three-carbon atom chain is preceded by the detachment of the carbamide group, which undergoes no further change. The three acids derivable from the central axis of the uric acid molecule, namely, malonic, tartronic, and mesoxalic acids, undergo fermentation by the uric acid bacterium with different degrees of rapidity, malonic acid being least readily destroyed, and mesoxalic acid most readily.

T. H. P.

Hydrogen Peroxide in the Nascent State. Bactericidal Action on Microbes in Water. EDMOND BONJEAN (*Compt. rend.*, 1905, **140**, 50—52. Compare Abstr., 1903, ii, 319).—The amount of hydrogen peroxide required to sterilise a litre of Seine water was found to be 0.291 gram, the time being 6 hours. A much smaller amount (0.060 gram) of nascent hydrogen peroxide, from calcium peroxide, sterilised the water in 4 hours.

N. H. J. M.

Action of Magnesium and of Magnesia on Microbes. F. DIENERT (*Compt. rend.*, 1905, **140**, 273—275. Compare Abstr., 1903, ii, 447).—The addition of magnesium to water containing micro-organisms (Eberth's bacillus and *Bacillus coli communis*) kills the bacteria after two or three days, whilst pure magnesia under similar conditions has no destructive action on the organisms, although its presence in a culture of the bacilli retards their growth; if, however, the oxygen of the air be displaced by hydrogen or a vacuum be made over water containing micro-organisms, it is rendered sterile in two or three days.

M. A. W.

Chemotaxis of Isoetes Spermatozooids. K. SHIBATA (*Chem. Centr.*, 1905, i, 266—267; from *Ber. Deut. bot. Ges.*, **22**, 478).—The normal salts of malic acid and its optical isomerides at concentrations of $N/20000$ and upwards exercise a powerful attraction on the spermatozooids of *Isoetes*. Normal succinates, fumarates, and tartrates act similarly, but less powerfully, whilst maleic and aminosuccinic acids, ethyl malate, and succinimide are without action. The sensibility is diminished by prior excitement. Free malic acid acts like the salts in very dilute solution, but repulsive effect increases with increasing concentration. The "critical concentration" at which the attractive force of a $N/1000$ solution of sodium malate is just overcome is equivalent for mineral acids, organic acids also acting in proportion to the number of hydrogen ions. The negative chemotaxis of these ions is thus shown, hydroxyl ions behaving similarly. There is an optimum concentration for the malic ions, as also for other di- and tri-basic

organic acids, above which the attraction begins to change to a repulsion. The ions of various heavy metals cause a negative action.

Since the critical concentrations of alkali and alkaline-earth nitrates and sulphates are not isotonic, and since all substances, which do not act in a negative sense, produce no repulsion in any concentration, it would appear that there is no osmotaxic excitability.

The sensibility towards sodium malate is destroyed by ether, chloroform, or chloral hydrate, and is destroyed or diminished by some electrolytes.

There appears with the *Isoetes* spermatozoids to be phototaxis along with a typical topotaxis. G. D. L.

Acidity of Plant Roots. CARLO MONTANARI (*Chem. Centr.*, 1905, i, 35; from *Staz. sper. agrar. ital.*, 37, 806—809. Compare Kohn, *Abstr.*, 1899, ii, 791).—The coloration observed by Kohn is only apparent, and similar results are obtained without roots. The reddening of litmus paper in contact with sugar beet roots is attributed to diffusion of the root acid. N. H. J. M.

Chlorophyllic Assimilation in Absence of Oxygen. JEAN FRIEDEL (*Compt. rend.*, 1905, 140, 169—170. Compare *Abstr.*, 1903, ii, 171).—Chlorophyllic assimilation was found to be not appreciably altered by decreasing the amount of oxygen to 2 per cent. It is now shown that assimilation takes place when the atmosphere does not contain any oxygen at all. When a leaf of *Euonymus japonicus* was exposed to light in a tube containing carbon dioxide (17·89) and nitrogen (82·11 per cent.), oxygen was liberated and carbon dioxide was absorbed. After about 6 hours, the atmosphere of the tube contained 0·48 per cent. of carbon dioxide, 18·70 per cent. of oxygen, and 80·81 per cent. of nitrogen. N. H. J. M.

Assimilation of Carbon by Plants. I. Supposed Formation of Formaldehyde. GIUSEPPE PLANCHER and C. RAVENNA (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 459—465).—The authors discuss the evidence which has been brought forward in favour of the preliminary formation of formaldehyde in the manufacture of starch by chlorophyll-containing plants. Experiments made on the distillation of extracts of leaves give no indication of the presence of either free or combined formaldehyde in the green tissues during the assimilation. T. H. P.

Forcing Experiments with Shrubs by means of Ether or Chloroform. O. DRUDE, A. NEUMANN, and FRANZ LEDIEN (*Bied. Centr.*, 1905, 34, 33—35; from *Zeit. Obst. Gartenbau K. Sachsen.*, 1904).—Experiments with two varieties of *Syringa* kept for 3 days at -4° showed that no accelerating action had taken place.

As regards the effect of ether, it was found that with a high temperature less ether need be employed. A second application of ether was found to be injurious. The favourable effect of ether ceases as the end of the year approaches, and by the end of November it may even be injurious. Plants etherised in the spring and kept in the

cold developed very few or no flowers, owing to the absence of the necessary reserve substances which would have accumulated during the period of rest of which the plants had been deprived.

The best amount of ether is 50 grams per hectolitre of air ; 75 grams are injurious, and 100 grams fatal. Chloroform is uncertain in its action, but gives good results if carefully employed. N. H. J. M.

Psidium Guayava (Djamboe) Leaves. A. ALTAN (*Chem. Centr.*, 1905, i, 265 ; from *Pharm. Post*, 37, 713).—The leaves have the percentage composition: resin, 3.15 ; fat, 5.99 ; volatile oil, 0.365 ; chlorophyll, 0.395 ; tannin, 9.15 ; mineral salts, 3.95 ; cellulose, 77.

The citron-yellow aromatic resin dissolves easily in chloroform, ether, or alcohol, melts at 189°, and has the iodine number 115, acid number 89, and saponification number 131. Alkalis colour it yellowish-red, and strong sulphuric acid produces a brown mass. The fat is yellowish-green, has a pleasant aromatic odour, and dissolves completely in chloroform, partially in ether or alcohol ; it melts at 235° and has an iodine number 199, acid number 95, and saponification number 137.

The greenish-yellow volatile oil contains eugenol and dissolves in chloroform, ether, or alcohol ; it boils at 237° and has a sp. gr. 1.069. Sulphuric acid colours it dark green, and bromine vapour orange-yellow. The tannin forms a brown, amorphous powder, soluble in water and alcohol, giving a black precipitate with iron salts and reducing alkaline copper solution after boiling with dilute sulphuric acid. Calcium and manganese are present in the plant in combination with phosphoric, oxalic, and malic acids. G. D. L.

Lactolase, an Enzyme causing the Formation of Lactic Acid in Plant Cells. JULIUS STOKLASA (*Chem. Centr.*, 1905, i, 265 ; from *Ber. Deut. bot. Ges.*, 22, 460).—The crude enzyme from the sap of the beet-root, potato, or pea causes vigorous alcoholic fermentation and the formation of lactic acid in dextrose solutions in the presence of 1 to 2 per cent. of toluene. This enzyme causes the formation of lactic acid during the respiration of the above plants and of the cucumber in the absence of micro-organisms.

When air has free access, and when the fermentation of the dextrose lasts more than 24 hours, hydrogen is evolved. The alcohol is oxidised by an enzyme to acetic acid, and at the same time formic acid is produced, and gives hydrogen and carbon dioxide. This hydrogen in the nascent state probably plays an important rôle in carbon dioxide assimilation by the chlorophyll-containing cells. G. D. L.

Chemical Examination of Cascara Bark. HOOPER A. D. JOWETT (*Reprint from Amer. Pharm. Assoc.*, 1904, 1—24).—An examination has been made of two samples of the bark of *Rhamnus purshianus*, one of which was comparatively fresh whilst the other was a commercial specimen which had been collected not less than three years previously. A specimen of the bark of *R. californicus* was also investigated. Each sample of bark gave practically the same results, which are summarised below.

The bark contains emodin together with a small quantity of an

isomeride which melts at 183° , but differs from emodin in being soluble in ammonia, and is possibly identical with *isoemodin* obtained from the bark of *Rhamnus frangula* (Thorpe and Miller, Trans., 1892, **61**, 6); its *acetyl* derivative melts at 168° . Dextrose was found in the bark, and a substance which on hydrolysis with dilute sulphuric acid yields syringic acid, but no evidence could be obtained of the presence of chrysophanic acid, chrysarobin, or of glucosides yielding, on hydrolysis, emodin, chrysophanic acid, or rhamnetin, Schwabe's conclusions (Abstr., 1889, 68) being thus confirmed. Neither the "cascarine" of Le Prince (*Compt. rend.*, 1892, **115**, 286) nor the "purshianin" of Dohme and Engelhardt (Abstr., 1898, ii, 629) could be isolated, and there can be no doubt that these substances were impure products. No substance corresponding with the crystalline material described by Prescott (*Amer. J. Pharm.*, 1879, **51**, 165) could be obtained from the bark.

Cascara bark contains about 2 per cent. of a fat consisting of rhamnol arachidate, arachidic acid, and certain substances, probably glycerides, which on hydrolysis furnish linolic and myristic acids. Rhamnol, $C_{20}H_{34}O$, is identical with the alcohol obtained by Power and Lees (Abstr., 1903, i, 773) from the seeds of *Brucea sumatrana*; it crystallises in white needles, melts at 135 — 136° , has $[\alpha]_D - 31^{\circ}$ in chloroform at 22° , and is readily soluble in ether, chloroform, benzene, or hot alcohol, and sparingly so in cold alcohol, acetone, water, or glacial acetic acid; its *acetyl* derivative melts at 117° .

An enzyme was isolated from the bark which is capable of effecting the hydrolysis of amygdalin.

A series of physiological experiments was carried out, the results of which indicated that the active principle of the drug was contained in the product obtained by adding basic lead acetate to an aqueous solution of the alcoholic extract, which had been previously treated with lead acetate and filtered, submitting the precipitate to the action of hydrogen sulphide and extracting the product with ethyl acetate. On evaporation, the ethyl acetate solution yielded a dark red residue, readily soluble in alcohol or water, but no crystalline substance could be isolated.

E. G.

Pigments of the Purple Pitcher Plant. GUSTAVE M. MEYER and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1904, xxxiii—xxxiv; *Amer. J. Physiol.*, **13**).—Alcohol extracts three colouring matters from the macerated pitchers of *Sarracenia purpurea*, namely, chlorophyll, alkaverdin (a purplish-red), and a brownish-black pigment. The solubilities of these substances are described, but their chemical relationships are not yet determined.

W. D. H.

Action of Sulphur Dioxide, Zinc Oxide, and Zinc Sulphate on Soils and Plants. EMIL HASELHOFF (*Bied. Centr.*, 1905, **34**, 31—33; from *Jahresb. landw. Versuchs-Stat. Marburg*, 1903—1904, 4).—Sulphur dioxide does not injure soils and is rapidly converted into sulphuric acid. Zinc oxide (0.2 per cent.) has a slight effect on the production of wheat when applied alone. In conjunction with lime, there is a greater reduction in the yield. Zinc sulphate in similar

amounts is found to be extremely injurious and its action is not diminished by the application of calcium carbonate. N. H. J. M.

Proteids of Wheat. I. The Proteid Soluble in Alcohol. THOMAS B. OSBORNE and ISAAC F. HARRIS (*Amer. J. Physiol.*, 1905, 13, 35—44).—Kutscher's determinations of glutamic acid are considered to afford no evidence that the proteid soluble in alcohol, obtained from the wheat kernel, consists of two distinct proteids. This proteid is probably a single substance; it should be called gliadin, and it is remarkable for the large amount of glutamic acid it yields. The amount is far in excess of that obtained from any other known proteid, and this fact deserves further study in view of the importance of wheat as a food. W. D. H.

Increase in the Weights of the Organic and Mineral Substances of Oats as a Function of the Age. MLLE. M. STEFANOWSKA (*Compt. rend.*, 1905, 140, 58—60).—It was previously shown (*ibid.*, 1904, 138) that the curve of increase in weight of the fresh substance of several plants is a hyperbola. In the present paper, curves are given for the increase of fresh substance, dry matter, and nitrogen in oats, and calculations have been made for constructing the curves for nitrogen, lime, phosphoric acid, potash, and iron.

Comparing fresh substance, dry substance, and ash, it is seen that the curves have the same general character in the first period of growth. Later on, the fresh substance becomes lower owing to loss of water, but the dry matter continues as before. N. H. J. M.

Movement of Nitrogenous Compounds and Pentoses in Beet Products during Fabrication. O. KOPETZKI (*Bied. Centr.*, 1905, 34, 56—65).—Determinations were made of the nitrogen in different forms, the sugar, and furfuroids in the various sugar-beet products. The furfuroids remain for the most part in the extracted sections and the amounts diminish at each stage to the last saturation. N. H. J. M.

Influence of Soil Moisture on the Amounts of Total and Proteid Nitrogen in Oat Straw. CONRAD VON SEELHORST and FRESSENIUS (*J. Landw.*, 1905, 53, 27—28).—The results of pot experiments in which the moisture of the soil was 55, 70, and 85 per cent. showed that, as the moisture increases, the proteid nitrogen diminishes less than the total nitrogen, and that the digestible proteid nitrogen diminishes more than the total proteid nitrogen.

In a dry season, the food value of straw will be higher than in a wet season. N. H. J. M.

Denitrification of Soil. III. GASPAR E. AMPOLA (*Gazzetta*, 1904, 34, ii, 301—315. Compare *Abstr.*, 1901, ii, 524; 1904, ii, 139).—The author's results lead to the following conclusions: manuring with nitrates of calcium and sodium gives a better result than without nitrate, whilst with calcium nitrate a larger yield is obtained than with sodium nitrate. Green material gives better results as manure than ripe stable manure, the latter better than fresh stable manure, and this again better than straw. The general con-

clusion, which confirms the results formerly arrived at (*loc. cit.*), is that calcium nitrate, the natural product of nitrification, is a better manure than sodium nitrate; further, the calcium salt offers a greater resistance to the action of denitrifying organisms than the sodium one, and this denitrification depends on the organic substances of the manure.

The author is in agreement with the view expressed by other investigators that the dangers of denitrification in the soil may be wholly or partially obviated by applying the nitrates only when the organic substances have been decomposed, that is, when the denitrifying bacteria have been reduced to inaction. T. H. P.

Employment of Dyes in Soil Investigation. B. SJOLLEMA (*J. Landw.*, 1905, 53, 67—69).—The amount of colloids in soils may be approximately estimated by treatment with a solution of methyl-violet (0.1—0.2 gram in 500 c.c.), which dyes the colloids but not the quartz, and examining with a microscope.

Experiments with different dyes and various colloids gave the following results: amorphous silica is coloured by methyl-violet, but not by naphthol-yellow, Congo-red, or alizarin. Aluminium silicate is coloured by methyl-violet and alizarin, not by Congo-red or naphthol-yellow. Alumina is coloured by all four dyes. Kaolin remained almost entirely colourless, only a very small portion of it fixing the different dyes. N. H. J. M.

Isolation of the Colloid Substances of Soils. B. SJOLLEMA (*J. Landw.*, 1905, 53, 70—76).—The soil is rubbed in a mortar with water several times, the water being poured off each time, evaporated nearly to dryness on a water-bath, and finally dried in a desiccator. The residue from the water is then centrifugalised in a mixture of bromoform and chloroform of sp. gr. 2.5 for two or three minutes. The liquid is poured off, filtered, and the residue on the filter washed with ether and dried. The whole process is repeated, a mixture of bromoform and chloroform having a lower sp. gr. (about 2.32) being employed. Treatment of the residue with methyl-violet and examination with a microscope (see preceding abstract) will give an idea as to the amount of sand still present.

A sample obtained in the manner described was treated successively with hydrochloric acid of sp. gr. 1.05 for 1 hour at 60°, with boiling 25 per cent. hydrochloric acid for 1 hour, and with sulphuric acid (2 parts to 1 part water) to decompose the kaolin. The undissolved portion consisted chiefly of quartz. The results show that the sample contained about 20 per cent. of kaolin and about 60 per cent. of silicates soluble in hydrochloric acid. Altogether about 95 per cent. of the constituents could be accounted for, and the remaining 5 per cent. consisted partly of phosphoric acid which was not determined.

N. H. J. M.

Manuring as based on Ten Years' Experiments. CONRAD VON SEELHORST (*J. Landw.*, 1904, 53, 29—60).—The results of

ten years' experiments on the same land with different cereals, mangels, potatoes, peas, and beans, are summarised. The large number of results are, however, insufficient to explain the manner in which the different climatic factors influence the crop. In the case of cereals and peas, the results show certain relations between weather and yields, but exceptions occur which cannot be accounted for with certainty.

N. H. J. M.

Employment of Calcium Cyanamide as Manure. RENATO PEROTTI (*Chem. Centr.*, 1905, ii, 117; from *Staz. sper. agrar. ital.*, 37, 787—805).—In order to avoid injury to seed, the manure should be applied some time beforehand, according to the character of the soil. The manure is favourable to early ripening.

N. H. J. M.

Manurial Experiments with Calcium Cyanamide and Garden Plants. RICHARD OTTO (*Chem. Centr.*, 1905, ii, 117; from *Gartenflora*, 1904).—Calcium cyanamide was found to be equal to nitrates and ammonium salts in the case of spinach, although at first growth was somewhat retarded. Equally satisfactory results were obtained with lettuce when planted twelve days after manuring.

The results of pot experiments showed that calcium cyanamide gave better results with white cabbage and maize than sodium nitrate. The manure seems to be suitable for garden plants provided that it is applied a week or two before planting, or else dug in to a depth of 13—26 cm.

N. H. J. M.

Injurious Action of Ammonium Thiocyanate [on Seeds and Plants]. EMIL HASELHOFF (*Bied. Centr.*, 1905, 34, 24—25; from *Jahresb. landw. Versuchs-Stat. Marburg*, 1903—1904, 3).—The crude manure, gas phosphate, obtained by purifying coal gas with superphosphate, contains large amounts (14·6 per cent.) of ammonium thiocyanate, most of which can be removed by washing with a concentrated solution of ammonium sulphate. The purified manure, however, still contains some thiocyanate (0·76 per cent.).

The results of germination experiments with red clover and mustard showed that even 0·0025 per cent. of ammonium thiocyanate retards germination, whilst with 0·1 per cent. germination was almost completely checked.

In pot experiments with oats, wheat, and mustard, it was found that 0·1 gram of ammonium thiocyanate (in 8·5 kilos. of soil) reduced the yield to 14·8 per cent., or in presence of calcium carbonate to 33 per cent. With 0·2 gram, there was scarcely any yield, and this amount is injurious even when applied twelve weeks before sowing. The purified substance is therefore useless as manure.

N. H. J. M.

The Agricultural Value of Humus Matter. J. DUMONT (*Compt. rend.*, 1905, 140, 256—258. Compare *Abstr.*, 1904, ii, 637).—Comparative experiments on the relative agricultural values of humic manure, mineral phosphates, and ordinary manure show that in the cases of sugar-beet, potatoes, maize, and lucerne a larger yield was obtained with the humic manure than with either of the other two,

the superiority being due to the humo-phosphates, which yield phosphoric acid more readily than do the mineral superphosphates.

M. A. W.

Action of Crude and Pure Potassium Salts with Calcium in Different Forms. WILHELM SCHNEIDEWIND and O. RINGLEBEN (*Bied. Centr.*, 1905, **34**, 12—18; from *Landw. Jahrb.*, 1904, **33**, 353. Compare Abstr., 1904, ii, 765 and 769).—Cereals and beet are benefited by the sodium chloride and other salts present in kainite, which should be employed unless the formation of crusts is likely to occur. For potatoes, 40 per cent. potassium salts are preferable. N. H. J. M.

[Manurial] **Action of Different Forms of Calcium and Magnesium.** DIEDRICH MEYER (*Bied. Centr.*, 1905, **34**, 18—24; from *Landw. Jahrb.*, 1904, **33**, 371. Compare Abstr., 1902, ii, 44).—When a soil is deficient in lime, both lime and magnesia are beneficial. When sufficient lime is present and the amounts of magnesia vary, no effect is produced by adding lime or magnesia unless the amounts applied are large. The lime requirements of soils must be judged by the amount of calcium present, except in the very rare cases in which the soil contains large amounts of magnesium.

N. H. J. M.

Analytical Chemistry.

Report from Committee on Uniformity in Analysis. I. [WILLIAM F. HILLEBRAND, CHARLES B. DUDLEY, HENRY N. STOKES, CLIFFORD RICHARDSON] (*J. Amer. Chem. Soc.*, 1904, **26**, 1644—1653).—A statement of the objects of the Committee on Uniformity in Chemical Analysis and of the policy it has adopted for the guidance of its work. L. DE K.

Statement of Analytical Results. WILHELM FRESSENIUS (*Zeit. anal. Chem.*, 1905, **44**, 32—36).—At the 5th International Congress for Applied Chemistry, held at Berlin, the first three of the following proposals were unanimously adopted, the fourth being referred back to the Analytical Committee for further consideration of the expression “ionand.” This expression, suggested by the author, is intended as a substitute for “ion” in cases where ionisation does not occur (for example, in a solid substance).

1. In all cases of statement of analytical results, the name should be followed by the formula.

2. By the name of an acid, the acid itself and neither its anhydride nor its ion is to be understood.

3. When results are calculated in the form of metal oxide and acid anhydride, the latter should be written thus :

Sulphuric acid (—anhydride) SO_3 , or

Sulphuric acid (calculated as anhydride) SO_3 .

4. When stated as ions or ionands, the metals should be cited by their names, distinguishing degrees of oxidation thus: mercurio-ion (or ionand), mercuri-ion (or ionand), and the anions or anionands as sulphate-ion (or sulphate-ionand) (SO_4), &c. M. J. S.

Use of the Micro-balance in Analysis. O. BRILL (*Ber.*, 1905, 38, 140—146. Compare Nernst and Riesenfeld, *Abstr.*, 1903, ii, 571; Jänecke, this vol., ii, 66).—In order to obtain accurate results with the micro-balance, attention to the following points is necessary. Where cement is used in its construction, celluloid or sealing wax is better than water-glass, which is hygroscopic; to avoid errors due to adhesion or to parallax, the indicator must be 2—3 mm. from the scale; the weights and pans must hang freely on the hooks; the balance must not stand on wood; the swing should extend to 80—100 scale divisions; with a greater swing, the balance is less sensitive. The micro-balance is to be recommended when simple analytical processes have to be accomplished rapidly, when only a small quantity of a substance is available, when a hygroscopic substance is analysed, and when the weighings must be carried out at a certain temperature.

Various estimations are quoted to show that accordant results can be obtained by it, although the quantities employed are only 1—2 mg. G. Y.

Use of the Rotating Anode in Electro-analysis. EDGAR F. SMITH [with GEORGE H. WEST and LILY G. KOLLOCK] (*J. Amer. Chem. Soc.*, 1904, 26, 1595—1615).—A number of experiments in which a rotating anode has been successfully employed in the electric precipitation of nickel and cobalt in the presence of various electrolytes such as ammonium acetate, sodium acetate, ammonia and ammonium sulphate, sodium formate, ammonium lactate, sodium lactate, and ammonium succinate. The results are illustrated by curves.

Favourable results are anticipated from the joint use of a rotating anode with a mercury cathode. L. DE K.

Testing Glass Vessels as to Neutrality. E. BARONI (*Chem. Centr.*, 1905, i, 43; from *Giorn. Farm. Chim.*, 1904, 53, 481—482).—The vessels are filled respectively with a 1 per cent. solution of morphine hydrochloride, a 0.5 per cent. solution of strychnine hydrochloride, and a 1 per cent. solution of mercuric chloride, and heated for half-an-hour in an autoclave at 112°. If after that time no change has taken place, the glass may be said to yield no alkali to water. If it does so, the morphine solution gives a brown, alkaloidal deposit, the strychnine solution also deposits free alkaloid, whilst the mercury solution deposits yellow, red, or brown oxides. L. DE K.

Table for the Preparation of Normal Solutions of Hydrochloric Acid according to the Density. FRIEDRICH W. KÜSTER and SIEGMAR MÜNCH (*Ber.*, 1905, 38, 150—152. Compare *Abstr.*, 1903, ii, 98).—The authors give directions for the determination, to

within ± 0.0001 , of the sp. gr. of solutions of hydrochloric acid by means of the 100 c.c. pipette and the analytical balance. A table is given, for the dilution to normal, of solutions of hydrochloric acid of sp. gr. 1.0500—1.1400 at 18°.

G. Y.

The Mechanism of the Guaiacum Reaction. NEUMANN-WENDER (*Chem. Centr.*, 1905, i, 122; from *Österr. Chem. Zeit.*, 7, 533—536).—The blue coloration is due to the oxidation by active oxygen of guaiaconic acid, with formation of an ozonide. The active oxygen is generated by the decomposition of hydrogen peroxide or an organic peroxide. This may be formed by the auto-oxidation of a component of the resin, or through the agency of an enzyme or enzyme compound (peroxydase, oxygenase).

L. DE K.

Colorimetric Estimation of Hydrogen Peroxide. PAUL PLANÈS (*J. Pharm. Chim.*, 1904, [vi], 20, 538—541).—In acid solution, hydrogen peroxide reacts on potassium iodide, iodine being set free, according to the equation: $2KI + H_2O_2 + H_2SO_4 = K_2SO_4 + 2H_2O + I_2$. Therefore, 0.022857 gram of iodine corresponds with 1 c.c. of oxygen, or 1 gram of iodine with 43.75 c.c. of oxygen. The quantity of iodine liberated may be estimated by treating a 10 per cent. solution of the hydrogen peroxide with 12 c.c. of a 10 per cent. solution of potassium iodide and 4 c.c. of an 8 per cent. solution of sulphuric acid, and comparing the coloration produced with that yielded by known quantities of a *N*/10 solution of iodine.

W. P. S.

Some Sources of Error in Sulphur Estimations. JOHN PATINSON and JOHN T. DUNN (*J. Soc. Chem. Ind.*, 1905, 24, 10—11).—Red india-rubber bungs, such as are used for wash-bottles, sometimes yield up sulphuric acid to water, especially when acted on by boiling water or steam. This sulphuric acid is probably due to the oxidation of the sulphur used for vulcanising or of metallic sulphides which have been added to the india-rubber. The authors have also found appreciable quantities of sulphur compounds in commercial samples of barium chloride.

W. P. S.

Estimation of Sulphur in Pyrites by Lunge's Method. (THE LATE) H. SALVIN PATINSON (*J. Soc. Chem. Ind.*, 1905, 24, 7—10).—In this method, the presence or absence of ammonium chloride, within the limits usually obtaining, has apparently no influence on the retention of chlorides by the barium sulphate or on the character of the precipitate of the latter. The degree of acidity, however, has an important effect. With less than 0.17 c.c. of hydrochloric acid per 100 c.c. of liquid, the precipitate retains barium chloride and is very fine. About 0.3 c.c. of hydrochloric acid per 100 c.c. gives the best results. With regard to the excess of ammonia necessary to be added to precipitate the ferric hydroxide and to prevent the formation of basic ferric sulphate, it is advisable to add an excess of at least 5 c.c. of ammonia of sp. gr. 0.88 at whatever temperature the precipitation and filtration be carried out. The most accurate results are obtained by precipitating the ferric hydroxide at a temperature of 70° and keeping the mixture

at this temperature for 15 minutes before filtering. The presence of ammonium chloride in considerable amount has but little effect on the solubility of barium sulphate.

W. P. S.

Iodometric Estimation of Sulphurous Acid in Alkaline Solution. OTTO RUFF and WILLI JEROCH (*Ber.*, 1905, **38**, 409—419).—In the estimation of sulphurous acid by addition of sodium hydrogen carbonate and an excess of iodine solution and titration with sodium thiosulphate (Rupp, *Abstr.*, 1903, ii, 40), an error is caused by the partial oxidation of the thiosulphate to sulphate, owing to the presence of sodium hypiodite (compare Förster and Gyr, *Abstr.*, 1903, ii, 209). The low values obtained on direct titration with iodine are shown to be due to the oxidising action of air, the iodine ions acting as an accelerator. This action may be hindered by taking precautions to prevent the access of air to the solutions, and also by adding a negative catalytic agent, such as mannitol (Bigelow, *Abstr.*, 1898, ii, 506). In the method finally recommended, a measured volume of the sulphite solution, made up with air-free water, is saturated with sodium hydrogen carbonate, 10—20 per cent. of mannitol is added, and the solution is titrated with iodine in an atmosphere of carbon dioxide. The results are independent of the concentration of the sulphite.

C. H. D.

Analysis of Solutions of Hyposulphites. **Analysis of Formalin.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1311—1317).—The method proposed by the author for the estimation of hyposulphites in solution is based on the fact that when such a solution is mixed with an alkaline solution of mercury potassium iodide, metallic mercury is deposited as a grey powder, $\text{HgI}_2 \cdot 2\text{KI} + \text{Na}_2\text{S}_2\text{O}_4 + 4\text{NaOH} = \text{Hg} + 2\text{NaI} + 2\text{KI} + 2\text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$. The mercury deposited is filtered by means of an asbestos filter and well washed with water on the filter. The plug of asbestos, together with the mercury, is then placed in a solution of sodium hydroxide, which is subsequently mixed with a known volume of *N*/10 iodine solution. After the mercury has dissolved, the solution is acidified with hydrochloric acid and the excess of iodine which has not combined with the mercury is estimated by titration with *N*/10 sodium thiosulphate solution. From the quantity of iodine taken up by the mercury, the amount of hyposulphite can be calculated, since $2\text{I}:\text{Hg}:\text{Na}_2\text{S}_2\text{O}_4$; every c.c. of *N*/10 iodine corresponds with 0.0087 gram $\text{Na}_2\text{S}_2\text{O}_4$.

When a dilute solution of formaldehyde is mixed with an alkaline solution of mercury and potassium iodide, metallic mercury is deposited as an amorphous, grey powder, the reaction being $\text{HgI}_2 \cdot 2\text{KI} + 3\text{KOH} + \text{H} \cdot \text{CHO} = \text{Hg} + 2\text{KI} + \text{H} \cdot \text{CO}_2\text{K} + 2\text{H}_2\text{O}$. The mercury is filtered on to an asbestos filter and its amount estimated in the manner just described. Each c.c. of *N*/10 iodine solution combining with the mercury corresponds with 0.0015 gram of formaldehyde.

The solid "hyposulphite NF," put on the market about two years ago, consists of a mixture of the two compounds, $\text{CH}_2(\text{SO}_2\text{Na})_2$ and $\text{Na}_2\text{SO}_3 \cdot \text{ZnSO}_3$. The first of these two compounds possesses the same reducing properties as sodium hyposulphite and its quantity may be estimated by the mercury method described above. The reaction in

this case is represented by the equation $\text{CH}_3(\text{SO}_2\text{Na})_2 + 3\text{HgI}_2 + 9\text{KOH} = 3\text{Hg} + \text{H}\cdot\text{CO}_2\text{K} + 2\text{NaKSO}_3 + 6\text{KI} + 5\text{H}_2\text{O}$. T. H. P.

Frerich's Estimation of Tellurium. ALEXANDER GUTBIER and W. WAGENKNECHT (*J. pr. Chem.*, 1905, [ii], 71, 54—56. Compare Abstr., 1902, ii, 134, 254, 558, 653; 1903, ii, 100; Frerich, Abstr., 1903, ii, 41).—The reduction of the oxides of tellurium by means of sulphur dioxide in presence of potassium iodide cannot be used as a means of estimating tellurium, as a varying proportion of tellurium tetraiodide is always formed. G. Y.

Detection of Nitrogen in Organic Substances. V. CASTELLANA (*Gazzetta*, 1904, 34, ii, 357—360).—The substance to be tested is intimately mixed with sodium or potassium carbonate and powdered magnesium, and the mixture heated in a test tube or porcelain crucible or on platinum foil. The mass is tested for cyanide in the ordinary way. If the substance is a liquid, a few drops of it may be allowed to fall on to the mixture of carbonate and magnesium when these two substances are reacting vigorously. T. H. P.

Influence of Various Kinds of Glass on the Accuracy of Kjeldahl's Nitrogen Process. HANS SCHÖNEWALD and K. BARTLETT (*Chem. Centr.*, 1905, i, 47; from *Woch. Brauerei*, 21, 793—794).—Experiments showing that the only trustworthy condensers are those made of Jena glass, which yield practically no alkali to the distillate. L. DE K.

Analysis of Compounds containing Nitrogen in Union with Nitrogen by means of Kjeldahl's Method. CL. FLAMAND and BERNHARDT PRAGER (*Ber.*, 1905, 38, 559—560. Compare Dafert, Abstr., 1888, 85; Krüger, Abstr., 1894, ii, 258, 397).—Kjeldahl's method is applicable to azo-, azoxy-, and hydrazo-compounds which have been subjected to the following preliminary treatment.

0.15—0.2 gram of the substance to be analysed is mixed with 10 c.c. of alcohol, 0.5—1 gram of zinc dust, and 2—5 c.c. of concentrated hydrochloric acid of sp. gr. 1.19, and heated until decolorisation takes place. Ten c.c. of concentrated sulphuric acid and 0.5 gram of crystalline copper sulphate are then added and the mixture heated until white fumes are evolved. After addition of 6 grams of powdered potassium sulphate, the liquid is heated until it becomes clear and light green.

This method does not give accurate results with phenylhydrazine, benzylidenephénylhydrazine, and formazyl compounds. G. Y.

Estimation of Nitrogen in Barley. E. GLIMM (*Chem. Centr.*, 1905, i, 46; from *Woch. Brauerei*, 21, 723—724).—1.5—1.8 grams of whole barley are introduced into a large Kjeldahl flask, 1 drop of mercury is added, and then 18—20 c.c. of sulphuric acid, which is allowed to moisten the sides of the neck and the flask. Fifteen to twenty grams of potassium sulphate are added in such a manner that a considerable portion will adhere to the neck. The whole is then heated

in the usual manner for about an hour. The frothing which takes place at first is harmless, as the crystals of potassium sulphate which are constantly dropping down break up the lather. The ammonia formed is estimated as usual.

L. DE K.

Estimation of Nitrogen in Barley. NEUMANN (*Chem. Centr.*, 1905, i, 46; from *Woch. Brauerei*, 21, 724—725).—A criticism of Glimm's process (see preceding abstract). The boiling should be continued for at least 10—15 minutes after the mixture has become colourless. The author also thinks that the quantity of barley operated on cannot always represent a fair sample.

L. DE K.

Simplified Elementary Analysis. A Quick Method. MAXIMILIANO DENNSTEDT (*Chem. Zeit.*, 1905, 29, 52—54. Compare Abstr., 1903, ii, 103).—Details are given of a quick method for performing combustions in a rapid current of oxygen with the apparatus previously described.

A. McK.

Elementary Analysis by Dennstedt's Method. HUGO WEIL (*Ber.*, 1905, 38, 282—283).—A case is recorded in which the "active" platinum used in Dennstedt's method of combustion (Abstr., 1897, ii, 432; 1898, ii, 146) had its activity destroyed by the presence of tin in the substance analysed.

W. A. D.

Estimation of "Coke" and "Volatile Matter" in Coal. GEORGES ARTH (*Bull. Soc. Chim.*, 1905, [iii], 33, 127—129).—The author employs for this purpose a platinum crucible with a capsular lid from 5—6 mm. deep, carrying on its upper surface a platinum tube 4—5 mm. in diameter and 15 mm. long, which can be closed at its upper extremity by a platinum cap. The crucible is heated by a flame 28—30 cm. high, produced by a blowpipe worked by a pump, and is placed at a height of 10 cm. above the aperture of the blowpipe. At the commencement of the operation, the cap is placed on the tube, but as soon as a bright flame appears at the mouth of the tube the cap is removed and is replaced when the flame begins to die down. The heating is continued for about 1 minute after the flame has disappeared. The results obtained in this way are more uniform than those given by Muck's method and the "coke" more nearly approaches in composition that obtained on the large scale (compare Constam and Rougeot, *Zeit. angew. Chem.*, 1904, 17, 737).

T. A. H.

Estimation of Organic Carbon in Soils. J. H. PETTIT and T. O. SCHAUB (*J. Amer. Chem. Soc.*, 1904, 26, 1640—1642).—Two grams of the soil are mixed with 1 gram of magnesium powder and 10 grams of sodium peroxide and ignited in a Parr bomb. The residue then contains all the carbon as carbonate and the carbon dioxide is estimated as usual in a Hempel apparatus. As part of the magnesium is left in the metallic state, the gas evolved on acidifying will contain an admixture of hydrogen. Allowance is, of course, made for the presence of carbonates in the soils and reagents.

L. DE K.

Apparatus for the Estimation of Carbon in Iron by Eggertz's Method. HANS SCHUMACHER (*Chem. Zeit.*, 1905, 29, 35).—The apparatus (Fig. 1) consists of a doubly-graduated cylinder divided vertically by means of an opaline glass wall into two compartments of 20 c.c. capacity. The funnel-shaped spouts *a* and *b* admit the two liquids to be compared. The solution of the sample is introduced into *a*, which during the shaking is closed with the finger, whilst *b* contains the standard liquid and is closed with a cork. When using this apparatus, the difference in shade of colour is more easily noticed than with the ordinary apparatus used for this purpose.

Fig. 2 represents a similar arrangement suitable in case of a large number of analyses. The tube *a*, which contains the comparison liquid, has a flat opaline wall. The other tubes (*b*), which are made of plain glass, are filled with the liquids to be tested and then placed alongside *a*.

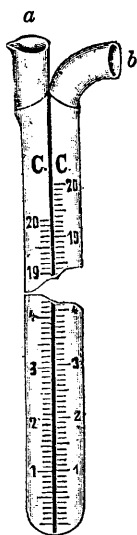


FIG. 1.

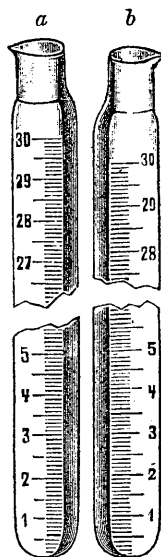


FIG. 2.

L. DE K.

Estimation of Carbon Monoxide in Confined Atmospheres. ALBERT LÉVY and A. PÉCOUL (*Compt. rend.*, 1905, i, 98—99).—The authors have devised a portable apparatus for estimating directly the carbon monoxide in the atmosphere of confined spaces; the method employed is due to Gautier and consists in collecting in chloroform the iodine liberated from iodine pentoxide by the reducing action of the carbon monoxide at 80°, and comparing the colour of the solution with those of a series of standard tubes containing solutions of iodine of known strengths. The reaction is sufficiently delicate to admit of the estimating of $\frac{1}{200000}$ of its volume of carbon monoxide in four litres of air.

M. A. W.

Indirect Estimation of Carbon Dioxide in Salts. O. LUTZ and A. TCHISCHIKOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1274—1281).—In the indirect estimation of carbon dioxide in salts by determining the loss of weight on fusion with potassium dichromate, &c., the authors recommend the use of sodium metaphosphate. This substance fuses at a low temperature, yields a thin liquid, and only requires about 20 minutes' fusion to expel all the carbon dioxide. The nitrogen pentoxide in nitrates may also be similarly determined by fusion with sodium metaphosphate. This method cannot be employed (1) when the base combined with the carbon dioxide is readily transformed, during the melting, into a higher state of oxidation by absorbing oxygen from the air (in some cases it may, however,

be used if the fusion is carried out in a stream of an indifferent gas), or (2) when the substance to be analysed contains other compounds volatile under the conditions of the experiment, such as the chlorides of the alkali metals; it may be used in such cases, however, to obtain the total volatile matter.

T. H. P.

Estimation of Potassium. FRIEDRICH KLINKERFUES (*Chem. Zeit.*, 1905, 29, 77—78).—Without troubling about the presence of sulphates or phosphates, a sufficiency of the solution is evaporated to dryness with addition of platinic chloride. The residue is slightly moistened with water and the excess of platinic chloride removed by repeated extraction with alcohol. The residue is then dissolved in boiling water and the filtered solution evaporated to dryness in a platinum dish with addition of a little formic acid. The reduced platinum adheres so firmly to the sides of the dish that it may be washed without the least loss with boiling water; in some cases, a further washing with 5 per cent. nitric acid is advisable. After gentle ignition, the crucible is cooled in a vacuum-desiccator and weighed and the weight calculated, say, to potassium oxide.

L. DE K.

Estimation of Potassium in Soils, Plants, and Fertilisers. FLETCHER P. VEITCH (*J. Amer. Chem. Soc.*, 1905, 27, 56—61).—Attention is called to the apparently forgotten, though excellent, process proposed by Moore, the main feature of which is the removal of any iron or aluminium chlorides by means of acidified alcohol (*Abstr.*, 1898, ii, 539).

L. DE K.

Separation of Silver from Lead. HJ. LIDHOLM (*Ber.*, 1905, 38, 566—568).—The mixture containing lead and silver is dissolved, the filtered solution neutralised, and sodium acetate added. If a precipitate of basic lead acetate is formed, it is dissolved by the addition of acetic acid and the solution boiled. On addition of a solution of quinol, the silver is immediately and quantitatively precipitated.

The presence of cadmium does not affect the separation. Copper, however, is partially reduced and partially precipitated as phenoxide. Bismuth is partially reduced. A modification of the method in those cases where copper or bismuth is present is described.

A. MCK.

Estimation of Calcium and Magnesium Carbonates. CARLO MONTANARI (*Chem. Centr.*, 1905, i, 48; *Staz. sperim. agrar. ital.*, 37, 810—814).—The estimation of calcium and magnesium carbonates in soils by heating with solution of ammonium nitrate (Frühling's process) is untrustworthy, as not only calcium sulphate but also calcium phosphate and calcium ortho- and di-silicates are more or less attacked.

L. DE K.

Technical Analysis of Cements. STEPHEN F. PECKHAM (*J. Amer. Chem. Soc.*, 1904, 26, 1636—1640).—Largely polemical in reference to papers by Hillebrand (*ibid.*, 25, 1180) and Blount (*Abstr.*, 1904, ii, 681).

L. DE K.

Detection of Small Quantities of Barium and Strontium. L. BLUM (*Zeit. anal. Chem.*, 1905, 44, 9—10).—In consequence of the tendency of ammonium sulphide to oxidation, barium and strontium may be entirely precipitated as sulphates together with the

sulphides of groups III and IV. It is therefore advisable to employ freshly prepared ammonium sulphide and to examine the nickel and cobalt sulphides for the alkaline earths. M. J. S.

Accuracy of the Dry Assay of Galena in an Iron Crucible. WILLIAM F. LOWE (*J. Soc. Chem. Ind.*, 1905, 24, 6—7).—The dry assay of galena is much more accurate than is generally supposed and for rich ores will give very good results. It is not suitable for poor ores, and for such a wet method should be used, but it can be used for most samples of dressed ore. Worked as follows, the method is stated to give results differing by only about 0.03 per cent. from the amount of lead actually present in the ore: 32.666 grams of ore (1 assay ton), 3 grams of potassium hydrogen tartrate, and 30 grams of sodium carbonate are mixed and placed in the front part of a bright copper scoop, 10 grams of crystallised borax being placed in the scoop behind the mixture. The whole charge is then shot into a red-hot wrought-iron crucible and placed in the furnace until the charge has run down and the surface is clear. The crucible is now shaken and its contents poured into a conical iron mould. Any particles of lead remaining in the crucible are collected by tapping it, run into another mould, and weighed with the large button. As soon as the flux has solidified, the button is separated, hammered, washed, dried, and weighed. The chief precaution is to remove the crucible from the furnace as soon as the reduction has taken place, usually in about 10 minutes; the temperature, also, must not be too high. W. P. S.

Aluminium as a Preventive of Acute and Chronic Mercury Poisoning. NAZARENO TARUGI (*Gazzetta*, 1904, 34, ii, 486—492).—Contrary to the generally accepted opinion, the efflorescence of aluminium amalgam does not require the presence of water, as it is produced when the amalgam is formed from mercury vapour and aluminium in dry air. The appearance of this efflorescence may be used as a means for detecting very minute quantities of mercury. On heating a mixture of a small quantity of a mercury salt with calcium oxide in a tube, to the open end of which is applied a thin sheet of aluminium, the latter becomes immediately coated with the amalgam. When a spiral of fairly stout aluminium wire is immersed for about ten minutes in a boiling dilute solution of mercuric chloride rendered slightly acid with sulphuric acid and is subsequently removed from the liquid, well dried by means of filter paper, and exposed to the air, in a few minutes the part which was immersed exhibits the fluorescence characteristic of aluminium amalgam. In this way, one-ten-millionth part of a milligram of mercury may be rendered apparent. No other metal exhibits such great capacity for fixing vapours of mercury or mercury compounds.

The author has constructed and patented a mask of fine aluminium gauze for the use of persons working in an atmosphere containing mercury vapour. Even though the air is saturated with mercury vapour, the latter is all absorbed by the aluminium and no symptoms of mercurial poisoning ensue. T. H. P.

Use of Tannic Acid in the Estimation of Alumina. ROBERT E. DIVINE (*J. Soc. Chem. Ind.*, 1905, 24, 11).—If to a solution containing approximately 0.1 gram of alumina 2 c.c. of a 2.5 per

cent. solution of tannic acid are added, then ammonia in slight excess, and the solution boiled until the odour has almost disappeared, the aluminium hydroxide is precipitated in a form which filters readily. This precipitate is also easily washed free from chlorides. The presence of tannic acid does not interfere with the subsequent separation of calcium and magnesium in the filtrate from the aluminium hydroxide should these be present, as in the analysis of clays, &c. Pure ferric hydroxide does not, however, filter satisfactorily in the presence of tannic acid. W. P. S.

Estimation of Manganese as Green Sulphide. JOHN C. OLSEN, E. S. CLOWES, and WILLIAM O. WEIDMANN (*J. Amer. Chem. Soc.*, 1904, 26, 1622—1627. Compare Abstr., 1903, ii, 372).—Ten c.c. of the solution supposed to contain about 0.15 gram of manganese are poured into 90 c.c. of boiling water containing 2.75 grams of ammonium chloride and five times the theoretical amount of ammonium sulphide, which should be free from polysulphide. After further heating for half-an-hour, the precipitation is complete, the green manganous sulphide is collected, washed with dilute ammonium sulphide, and dried. It is then converted into anhydrous sulphide by ignition with sulphur in a current of hydrogen, as usual. L. DE K.

Estimation of Manganese as Sulphide in Ores containing Barium. L. BLUM (*Zeit. anal. Chem.*, 1905, 44, 7—9).—In consequence of the liability of ammonium sulphide to oxidation, the manganese sulphide is always contaminated with barium sulphate and thiosulphate unless the barium has first been removed by adding a little sulphuric acid whilst separating iron and alumina as basic acetates. The same source of error exists in the separation of manganese and iron by the barium carbonate method. M. J. S.

Detection of Ferrous Oxide in Presence of Ferric Oxide. L. BLUM (*Zeit. anal. Chem.*, 1905, 44, 10—11).—The formation of the brown compound of nitric oxide and ferrous salts can be utilised in cases where the ferricyanide reaction is obscured by the presence of other metals. The solution to be tested is mixed with an equal volume of concentrated sulphuric acid, the mixture cooled, and a large fragment of potassium nitrate thrown in. The crystal becomes surrounded with characteristic reddish-brown streaks. If much chloride is present, this should be mainly converted into sulphate by boiling the mixture after adding the sulphuric acid. M. J. S.

Estimation of Iron in Blood by the Ferrometer. ADOLF JOLLES (*Zeit. anal. Chem.*, 1905, 44, 6—7).—A series of estimations of iron in blood, in which the results obtained by a volumetric process from 20 c.c. of blood were compared with those yielded by the author's "ferrometric" method (this vol., ii, 67), showed only insignificant differences. The necessity for employing the mean of several readings is insisted on. M. J. S.

Electrolytic Deposition of the more Important Metals from Moving Solutions. ARTHUR FISCHER and R. J. BODDAERT (*Zeit. Elektrochem.*, 1904, 10, 945—953).—The ordinary electrolytic methods of estimation of several metals are compared experimentally with the

methods using rapidly rotating electrodes, in order to discover how far the estimation can be shortened without sacrifice of accuracy. Except where otherwise noted, a matt platinum dish was used as cathode and a disc of platinum making up to 800 revolutions per minute as anode. The best conditions observed are as follows :

Nickel.—Cold saturated solution of ammonium oxalate, 6—7 volts, 8 amperes. Time for complete precipitation, 40 minutes, temperature 20—60°.

Zinc.—Good results are obtained with a solution containing sodium acetate and acetic acid, but the most satisfactory deposit was obtained from a strongly alkaline solution containing a little potassium cyanide. Five amperes and 5 to 5.4 volts were used, temperature 95°, time required 20 minutes.

Copper.—Good results are obtained with any of the usual solutions ; with a current of 5 amperes and working at 95°, the precipitation is complete in from 10 to 30 minutes according to the quantity of metal present. It is advisable to add ammonia when most of the copper is deposited and stop the current when the blue colour has disappeared.

Bismuth.—The metal is always deposited in a spongy condition, and trustworthy results cannot be obtained.

Cadmium.—Fairly good results were obtained by using a solution acidified with sulphuric acid ; with 5 amperes, 15—16 volts, and a temperature of 95°, the metal is deposited in 10—15 minutes, only the last part of it being spongy.

Lead.—The deposition of lead at the anode in the form of the peroxide is complete in 15 minutes at 95°, using 10 amperes and 3.5 volts. The precipitation is perfect.

Silver.—This metal is deposited from the solution in potassium cyanide with a current of 2 amperes and 4.5 volts at 95° in 10 to 15 minutes. The results are about 0.2 per cent. low.

Mercury is deposited from a solution in nitric acid ; the temperature must not be allowed to rise above 45°, otherwise mercury is volatilised. Using 4 amperes and 5.4—6 volts, the deposition is complete in 15 to 20 minutes.

Antimony.—The metal was used in the form of thioantimonate, polysulphides being removed by adding potassium cyanide. The results were, however, always low, especially with quinquevalent metal, probably owing to some of the antimony going to the anode in the form of a complex anion.

Tin.—The results were similar to those obtained with antimony, probably for the same reason.

In conclusion, the construction of a stand which permits the anode to be rotated and which has suitable electrical connections is described.

T. E.

Electrolytic Analysis of Cobalt and Nickel. F. MOLLWO PERKIN and W. C. PREBBLE (*Trans. Faraday Soc.*, 1905, 1, 103—109).—Cobalt is quantitatively separated as a bright metallic deposit by electrolysing a solution containing alkali phosphate and a small quantity of phosphoric acid, temperature 55—60°, current density

0.2—1.2 amperes, 2—4 volts. The addition of phosphoric acid is necessary to prevent the separation of alkali cobalt phosphate, but if present in too large quantity it retards very greatly the separation of the cobalt. Addition of hydroxylamine removes any deposited cobalt oxide from the anode during the early stages of the electrolysis. The cobalt deposits from solutions containing ammonium tartrate and oxalate were invariably too heavy; solutions containing ammonia and ammonium borate gave good results, but the deposit was brown.

The acid phosphate solutions were found unsatisfactory in the separation of nickel; excellent results were, however, obtained from solutions containing ammonia and ammonium borate. H. M. D.

Electrolysis of Cobalt and Nickel Tartrates. JAY E. ROOT (*J. Physical Chem.*, 1905, 9, 1—12).—The decomposition voltage for cobalt in alkaline tartrate solution is about 1.75 volts, that for nickel about 2.8 volts. It seems possible, therefore, that a quantitative separation would be possible electrolytically. It was found, however, that although, if the voltage be kept below 2.1 volts, the cobalt is deposited in a pure state, yet at higher voltages the cobalt deposited always contains nickel. At these lower voltages, complete separation is possible, but it is exceedingly slow, partly owing to the oxidation of cobaltous salts, and the addition of various reducing agents was not found to make the process satisfactory. It was found that cobalt alone in solution could be accurately determined by electrolysis. In one experiment, it was found that with 0.0870 gram metallic cobalt in solution 0.0802 gram was deposited on the cathode and 0.0122 gram of cobaltic oxide at the anode, the solution being free from cobalt. This weight of oxide corresponds very closely with the formula $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and confirms Coehn's results (*Abstr.*, 1903, ii, 80). L. M. J.

Combined Oxidimetric Method for the Estimation of Molybdenum Trioxide and Vanadium Pentoxide in Presence of One Another. BORIS GLASMANN (*Ber.*, 1905, 38, 600—603).—The separation described is based on the fact that vanadic acid in sulphuric acid solution is quantitatively reduced by zinc to vanadium dioxide, and by magnesium to vanadium trioxide, whilst molybdic acid in sulphuric acid solution is reduced by zinc or magnesium to molybdenum sesquioxide. The amounts of vanadic acid and molybdic acid in a mixture may be estimated by titrating the reduction product with potassium permanganate, when the changes involved are represented by the equations: (1) $5\text{V}_2\text{O}_5 + 5\text{Mo}_2\text{O}_3 + 15\text{O}_2 (= 12\text{KMnO}_4) = 5\text{V}_2\text{O}_3 + 10\text{MoO}_3$ and (2) $5\text{V}_2\text{O}_3 + 5\text{Mo}_2\text{O}_3 + 25\text{O} (= 10\text{KMnO}_4) = 5\text{V}_2\text{O}_5 + 10\text{MoO}_3$.

Equal volumes of a titrated solution of both acids were introduced into separate flasks, and the reduction conducted in one case with zinc and hydrochloric acid, and in the other with magnesium and hydrochloric acid. The resulting solutions were then separately mixed with a solution of manganese sulphate, and each solution titrated with standard permanganate. A. McK.

New Iodometric Estimation of Alkali Heptamolybdates. BORIS GLASMANN (*Ber.*, 1905, **38**, 193—194).—A warm aqueous solution of an alkali heptamolybdate readily precipitates iodine from the usual iodide-iodate mixture (*Abstr.*, 1904, ii, 214) owing to its hydrolysis into normal alkali molybdate and free molybdic acid, as represented by the equation $3(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 12\text{H}_2\text{O} = 9(\text{NH}_4)_2\text{MoO}_4 + 12\text{H}_2\text{MoO}_4$. The free molybdic acid reacts with the iodide-iodate mixture according to the equation $20\text{KI} + 4\text{KIO}_3 + 12\text{H}_2\text{MoO}_4 = 12\text{K}_2\text{MoO}_4 + 12\text{I}_2 + 12\text{H}_2\text{O}$. One gram of the crystallised ammonium heptamolybdate is thus equivalent to 0.822 gram of iodine. J. J. S.

Detection of Stannous Tin. L. BLUM (*Zeit. anal. Chem.*, 1905, **44**, 11—12).—In the absence of other reducing agents, stannous compounds can be detected by causing them to reduce ferric chloride and then proving the presence of ferrous iron by adding sulphuric acid and potassium nitrate (see this vol., ii, 206). A precipitate containing arsenic, antimony, and tin as sulphides may be examined for tin by boiling it with fuming hydrochloric acid until hydrogen sulphide is completely expelled, and then applying the test to the solution.

M. J. S.

Estimation of Methyl Alcohol in Formaldehyde. ROBERT GNEHM and FELIX KAUFLEDER (*Zeit. angew. Chem.*, 1905, **18**, 93).—The authors' process (*Abstr.*, 1904, ii, 520) having been adversely criticised by Bamberger, it is now stated that by raising the quantity of crystallised sodium sulphanilate from 90 to 110 grams, the process may also be used for very concentrated solutions of formaldehyde.

L. DE K.

Colour Reactions for Alcohols (excepting Methyl and Ethyl) and for Compounds of Alcoholic Function or Hydroxylic Compounds. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1905, [vi], 14—17).—The colorations are produced by mixing 1 c.c. of the alcohol with 5 or 6 drops of a saturated aqueous solution of furfuraldehyde, and then adding the same amount of concentrated sulphuric acid. With solids, a solution in ethyl alcohol may be used, or the substance may be first dissolved in the acid. A considerable number of mono- and poly-hydric alcohols and phenols, sugars, and hydroxy-acids were examined and the colours obtained are described, the latter being for the most part violet and red or brownish-violet. With cholesterol and anthesterol, the reaction (blue) is characteristic, being produced by a trace of substance in alcoholic solution. G. D. L.

Estimation of Phenol. S. J. LLOYD (*J. Amer. Chem. Soc.*, 1905, **27**, 16—24).—A modification of Koppeschaar's bromine process, so as to avoid several sources of error. The phenol solution is put into a stoppered flask, and a volume of hydrochloric acid is added equal to about one-fourth of the bulk of the liquid after adding the bromine solution. The bromine solution (9 c.c. bromine, 28 grams potassium hydroxide, water up to 2 litres) is added from a burette until the liquid turns yellow, when another tenth or fifth part of that already used is added. Excess of solution of potassium iodide

(17 grams in 100 c.c.) is added, the liquid is diluted with water (10 c.c. for each c.c. of acid added), and after adding 10 c.c. of chloroform the liberated iodine is titrated as usual, using *N*/50 sodium thiosulphate and starch as final indicator. The bromine solution is checked as usual with the thiosulphate, and from the difference in the two titrations the amount of phenol is calculated.

L. DE K.

Presence of Dextrose in Tannin Solutions. H. NOVÉ (*Chem. Centr.*, 1904, ii, 1765; from *Bull. Assoc. Chim. Sucr. Dist.*, 22, 325—326).—Even a concentrated alcoholic solution of tannin gradually undergoes a kind of fermentation with formation of dextrose, and is therefore not to be recommended in sugar analysis.

L. DE K.

Potassium Oxalate as a Lead Precipitant in Sugar Analysis. HARRIS E. SAWYER (*J. Amer. Chem. Soc.*, 1904, 26, 1631—1635).—Potassium oxalate is recommended for the removal of the excess of lead added for the purpose of classifying sugar solutions intended for polarimetric or chemical tests.

L. DE K.

Direct Estimation of Sugar in Beet by Pellet's Water Process: Influence of Air on the Results. HENRI PELLET and L. PELLETT (*Chem. Centr.*, 1904, ii, 1765; from *Bull. Assoc. Chim. Sucr. Dist.*, 22, 312—317).—A reply to Loga, who states that Pellett's process yields too high results unless care is taken to work in a vacuum. The authors find that the quantity of air left in the mass is too small to affect the results, particularly if care is taken to remove any froth by adding a few drops of ether and alcohol.

L. DE K.

Estimation of Methylpentosan in Presence of Pentosans. W. B. ELLETT and BERNHARD TOLLENS (*J. Landw.*, 1905, 53, 13—25).—Rhamnose can be determined by the method employed for pentosans. The aniline acetate test, is, however, unsuitable for methylfurfuraldehyde. A few drops of the distillate produce a yellowish-red coloration when a drop of phloroglucinol solution (in hydrochloric acid of sp. gr. 1.06) is added if methylfurfuraldehyde is present. With small amounts of rhamnose (to 0.15 gram), the distillation may be stopped after 300 or 350 c.c. have been distilled; with larger amounts, the distillate should amount to 400 c.c. or more.

The amount of rhamnose is calculated from the weight of phloroglucide (Pg) as follows:

$$\text{Rhamnose} = \text{Pg}, 1.65 - \text{Pg}^2, 1.84 + 0.010.$$

When pentosans and methylpentosans occur together, the dried mixture of phloroglucides is weighed and extracted in the Gooch crucible for 10 minutes with 15—20 c.c. of alcohol of 95° Tr. at about 60°. It is again dried and weighed. The second weight is that of the furfuraldehyde-phloroglucide, and the difference between the two weights the methylfurfuraldehyde-phloroglucide.

Results of actual determinations with mixtures of rhamnose and arabinose were not entirely satisfactory. They were, however, more

correct than would be the case if the whole of the phloroglucide were calculated as arabinose (or pentose).

Determinations of pentosans and of methylpentosan (as rhamnose) were made with a variety of substances. N. H. J. M.

Commercial Analysis of Formaldehyde. WILHELM FRESENIUS and LEO GRÜNIUT (*Zeit. anal. Chem.*, 1905, **44**, 13—24).—Of the numerous methods which have been proposed for the estimation of formaldehyde, four are in practical use, namely, Legler's ammonia and sodium hydroxide methods (Abstr., 1883, 1035), Blank and Finkenbeiner's hydrogen peroxide method (Abstr., 1899, ii, 188), and Romijn's iodimetric method (Abstr., 1897, ii, 166). The ammonia method is known to give results about 1—1.5 per cent. too low (compare Abstr., 1904, ii, 98, 299). The sodium hydroxide process is open to the objection that polymerisation of the aldehyde frequently occurs and impairs the accuracy of the results. The other two methods are free from inherent sources of error, but require certain modifications of the original form to ensure accuracy. In both methods, it is essential that the contact of the formaldehyde with sodium hydroxide should be as brief as possible before the addition of the oxidising reagent, since otherwise formic acid would result from the direct action of the alkali. It is even advisable (in Blank's method) to add a little hydrogen peroxide (5 c.c.) to the soda before bringing it in contact with the formalin, but the time prescribed for adding the whole quantity (50 c.c. in the course of 3 minutes) must not be shortened, nor must the mixture be cooled during the reaction. In Romijn's process, it is advisable to work on much larger quantities than originally prescribed, and in consequence of the smallness of the volume operated on (5 c.c.) it is absolutely necessary that the measurements should be made with great accuracy. The absence of iodate from the iodide and of nitrites from the sodium hydroxide must be ensured, and since the formalin may contain various impurities capable of absorbing iodine, no result should be accepted without the concordance of two distinct methods. M. J. S.

Quantitative Analysis of some New Surgical Dressings. WILHELM FRESENIUS and LEO GRÜNIUT (*Zeit. anal. Chem.*, 1905, **44**, 25—31).—*Vioform and Vioform Gauze*.—Chloroiodohydroxyquinoline, $C_9NH_4ClI \cdot OH$, introduced into commerce as a substitute for iodoform, is a light powder readily soluble in cold alcoholic potash. The solution may be boiled for several hours without material alteration. It remains clear when considerably diluted with water, and the vioform is reprecipitated quantitatively when the alkali is exactly neutralised with nitric acid. The gauze may therefore be analysed by soaking 6—8 grams of it with $N/2$ alcoholic potash for 2 hours in a Soxhlet extractor, washing out with boiling alcohol, diluting the solution with 10 vols. of water, neutralising with nitric acid, collecting the precipitate, washing, and weighing. An estimation of the halogens should be made to confirm the identity of the weighed precipitate.

Ektogan.—This substance consists essentially of zinc dioxide with some zinc oxide and carbonate. It dissolves without evolution of

oxygen in dilute mineral acids, and the amount of peroxide either in the substance itself or in gauze prepared with it may be estimated gasometrically by treating the solution (in sulphuric acid) with potassium permanganate and measuring the oxygen evolved.

M. J. S.

Estimation of the Volatile Acids in Wine. KARL WINDISCH and THEODOR ROETTGEN (*Zeit. Nahr. Genussm.*, 1905, 9, 70—81).—The total acidity is estimated on 25 c.c. of the wine; 25 c.c. of the wine are then evaporated in a china basin to a volume of 2—3 c.c., 25 c.c. of hot water are added, and again evaporated down to 3 c.c.; 25 c.c. of water are again added, and a third time evaporated. The residue is then dissolved in hot water and the solution titrated. The result, calculated into tartaric acid, is the non-volatile acidity. The difference between this and the total acidity, multiplied by 0.8, gives the volatile acidity expressed as acetic acid.

As in many wines lactic acid is often the principal acid present, the direct estimation of the volatile acids by distillation is rendered unsatisfactory owing to the partial volatility of the lactic acid. On distilling 50 c.c. of wine with steam, an acid distillate is still obtained after 200 c.c. of distillate have been collected. Carbon dioxide in the steam also introduces an error in the direct estimation, as does the tendency of lactic acid to form a neutral anhydride when subjected to heat.

W. P. S.

The Mean Molecular Weight of the Non-volatile Fatty Acids of Dutch Butter. A. OLIG and J. TILLMANS (*Zeit. Nahr. Genussm.*, 1904, 8, 728—730).—The authors find that the molecular weight of the non-volatile fatty acids of Dutch butter frequently exceeds 261 in summer, and is almost always higher than this figure in the autumn. Values were obtained in the months of August, September, and October varying from 257.8 to 271.6, the butters examined being prepared from the milk by the authors themselves. The molecular weight of the non-volatile fatty acids affords, therefore, little evidence of the presence of foreign fats in butter.

W. P. S.

Colour Reaction of Uric Acid with Phosphotungstic Acid; Preliminary Treatment of Urine before Estimating Urea. HENRI MOREIGNE (*Ann. Chim. anal.*, 1905, 1, 15).—A claim for priority, and also a reply to Frabot (*Abstr.*, 1904, ii, 844). The author still thinks that phosphotungstic acid is the best precipitant for uric acid in urines although the precipitation is not quite complete.

L. DE K.

Acidimetry of Animal Liquids. HANS FRIEDENTHAL (*Chem. Centr.*, 1904, ii, 1668—1669; from *Verh. Ges. Deut. Nkf. Aerzte*, 1903, ii, 441—442).—Acidimetric estimations by means of gas elements with platinum or palladium electrodes are not trustworthy. A colorimetric method with an indicator or indicators is made use of. Seventeen solutions of hydrions, varying from 2*N* to 5×10^{-15} gram

hydriions per litre are prepared, and each solution gives a characteristic colour with different indicators. The preparation of the standard solutions is accomplished by means of electrical conductivity determinations. When this indicator method is employed, the solutions must be such that other colorations are not present. The method is of use for homogeneous liquids only and not for cell protoplasm. Blood serum, blood plasma, saliva, kidney, urine with a fruit and vegetable diet, sea and spring water, and the fluids of various lower organisms have an acidity of from $2-5 \times 10^{-8}$ gram hydriions per litre. Stomatic juice, urine from carnivora, and the pancreatic excretion are more acidic, and many vegetable juices have a strong acidic reaction. $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ in concentrated solution act as a poison of living organisms.

J. J. S.

Halphen's Reaction. KARL FISCHER and H. PEYAU (*Zeit. Nahr. Genussm.*, 1905, 9, 81-90).—Experiments are described in which cotton-seed oils were subjected to various treatments with the object of ascertaining whether they could be made to give a negative reaction with Halphen's test. Heating the oil for 6 hours at temperatures up to 150° had little effect on the sensitiveness of the reaction. When heated for 6 hours at 250° , the oil ceased to give any coloration, but at the same time was rendered quite unedible. No change in the intensity of the coloration was observed when the oil tested had previously been treated with zinc and sulphuric acid or with 4 per cent. potassium hydroxide, either cold or at 100° . On the other hand, oils subjected to the action of sulphurous acid and afterwards washed with alcohol, to remove the free acids formed, ceased to give a coloration, whilst the refraction, iodine and saponification values of the oils remained practically unchanged.

W. P. S.

Estimation of Butter-fat and Cocoa-nut Oil in Margarine. AAGE KIRSCHNER (*Zeit. Nahr. Genussm.*, 1905, 9, 65-70).—The following method is a modification of the process previously published by K. Jensen (*Farm. Tid.*, 1903, 385). It is based on the precipitation of octoic acid by means of silver sulphate and is a continuation of the Reichert-Meissl process. The distillate obtained in the latter is filtered as usual, and 100 c.c. of the filtrate titrated with $N/10$ barium hydroxide solution. To the neutral solution, 0.5 gram of silver sulphate is added, the mixture shaken from time to time for 1 hour, and then filtered. One hundred c.c. of the filtrate are placed in a flask, 35 c.c. of water and 10 c.c. of dilute sulphuric acid are added, and the whole distilled until 110 c.c. of distillate have been collected. The latter is filtered, 100 c.c. of the filtrate are titrated with $N/10$ barium hydroxide, and the result calculated for 5 grams of fat. The number obtained is termed the "new value" or the second titration value. From the results of the analyses of a number of test-samples, the author shows that the amounts of butter-fat and cocoa-nut oil in margarine can be calculated from the two formulæ: percentage of butter-fat = $4.319, N.V. - 0.456, R - 2.15$, and percentage of cocoa-nut oil

$= 7.42R - 8.116N.V. - 3.57$, in which *N.V.* is the "new value" and *R* the Reichert-Meissl value of the sample. W. P. S.

Tobacco Oil. Chemical and Physical Properties and Composition. GASPARE AMPOLA and FRANCESCO SCURTI (*Gazzetta*, 1904, 34, ii, 315—321).—The yellow oil obtained by pressing (9—10 per cent.) or extracting (30—32 per cent.) the seeds of *Nicotiana tabacum* has a pleasant odour, and a sp. gr. 0.9232 at 15°; it thickens at -15°, solidifies to a yellow mass at -25°, dissolves in 31 parts of absolute alcohol, and mixes in all proportions with ether, carbon disulphide, chloroform, or oil of turpentine. It begins to boil at about 150° and inflames at 320—375°. With sulphuric acid (Heydenreich's reaction), it gives, if not shaken, a bright yellow coloration changing to reddish-brown; after shaking, the liquid becomes dark brown. With nitric acid (Bach's reaction), it gives a dirty-white coloration, which changes to yellowish-red after five minutes' heating; when left for 12—18 hours, the liquid assumes a buttery consistency. With Hauchecorne's reagent (3 parts of pure nitric acid of 40° B. and 1 part of water), it gives an intense red coloration after 20 minutes' heating on a water-bath. When subjected to Archbutt's modification of Poutet's elaidic test, the oil remains liquid but gives a white deposit. The thermal index, as determined in Tortelli's thermo-oleometer, is 100. The percentages of oxygen absorbed (Livache's method) after 2, 3, 4, and 14 days are 5.01, 5.61, 5.84, and 6.84 respectively. The acidity of the oil is 3.49 per cent. (as oleic acid), the saponification index 190, the saponification index of the fixed fatty acids 203, the mean molecular weight of the latter 275.8, the Helmer number 94.73, and the iodine number 118.6. The fatty acids present in the oil consist mainly of oleic acid (about 25 per cent.), linoleic acid (about 15 per cent.), and palmitic acid (about 32 per cent.), with small quantities of stearic acid. T. H. P.

Estimation of Rosin in Shellac. ARTHUR C. LANGMUIR (*J. Soc. Chem. Ind.*, 1905, 24, 12—17).—The author considers that the iodine absorption of a sample of shellac affords good evidence as regards the purity of the sample. From the values obtained with the best grades of commercial shellacs, it must be taken that shellacs free from rosin have an average iodine value of 18. Rosin, on the other hand, has an iodine value well above 200, with an average of 228. Wij's solution should be used for the estimation, and the absorption allowed to proceed for 1 hour. The following modification of the Storch-Morawski reaction is recommended as a qualitative test: 1 gram of the sample is gently heated with 15 c.c. of acetic anhydride and then cooled. Rosin remains in solution, whilst the greater part of the shellac separates as a gelatinous mass which is filtered off. The filtrate is collected in a test-tube and a few drops of sulphuric acid carefully introduced, agitating the filtrate a little as the acid meets it. An evanescent coloration is obtained with as little as 2 or 3 per cent. of rosin. A pure shellac gives no coloration if care be taken to avoid charring. W. P. S.

Estimation of Urea. O. WENTZKI (*Chem. Centr.*, 1904, ii, 1520—1521; from *Pharm. Zeit.*, 49, 898).—The apparatus consists of

a 30 c.c. flask with a short neck into which is ground a 10 c.c. stop-cock-pipette, the upper end of which may be connected by an india-rubber tube with a gas-burette. The apparatus, when filled, weighs about 50 grams. When testing urine, 2 c.c. of the sample and 5 c.c. of a 28 per cent. sodium hydroxide solution are introduced into the flask, the pipette filled with hypobromite solution is fixed on, and after connecting it with the burette the tap is turned and the liberated nitrogen collected.

If a gravimetric estimation is preferred, 5 c.c. of urine are used, and the apparatus is weighed before and after the reaction. L. DE K.

Detection of Archil, Cudbear, and other Lichen Colours. LUCIUS M. TOLMAN (*J. Amer. Chem. Soc.*, 1905, **27**, 25—26).—These colours may be mistaken for coal-tar dyes, as they also pass into amyl alcohol from an ammoniacal solution, and on evaporation of the alcohol leave a purple residue. This is, however, distinguished from coal-tar dyes by the fact that its aqueous solution is reduced by tin and hydrochloric acid, and then reoxidised by ferric chloride.

L. DE K.

Action of Various Physical and Chemical Agents on the Gluten of Wheat Flour. Estimation of Gluten. ÉMILE FLEURENT (*Bull. Soc. chim.*, 1905, [iii], **33**, 81—101. Compare Abstr., 1898, ii, 627; 1902, ii, 102; and Balland, Abstr., 1897, ii, 296).—A detailed study has been made of the various factors influencing the estimation of gluten in wheat flour by washing away the starch and soluble matters with water. It is shown that a portion of the gluten (probably the globulin) is lost when distilled water or natural waters containing calcium chloride or sulphate or sodium chloride are employed, and that the best results are secured by the use of water containing calcium hydrogen carbonate. The time occupied in the isolation of the gluten should not exceed 16 minutes, the temperature of the water employed should be about 16°, and there is no advantage in allowing the dough to stand for some time before washing (compare Balland, *loc. cit.*). The gluten should be dried at 105° before weighing (compare Arpin, Abstr., 1903, ii, 119). The difficulty of satisfactorily isolating the gluten is greater with sour flours, and it is advantageous in such cases to mix sodium hydrogen carbonate with the flour in order to neutralise the free acid. When the estimation is carried out with due observance of these precautions, concordant results are obtained, which are in close agreement with those given by more elaborate chemical methods (compare Arpin, *loc. cit.*). T. A. H.

Estimation of Catalases in Blood. ADOLF JOLLES (*Zeit. anal. Chem.*, 1905, **44**, 1—5).—By adopting standard conditions for the action of catalase on hydrogen peroxide, the amounts of the enzyme in different samples of blood can be compared, although the quantity of peroxide decomposed is not strictly proportional to that of catalase present. The blood (0.05 c.c.), immediately after it is drawn, is diluted to 50 c.c. with 0.9 per cent. sodium chloride solution. Of

this, 10 c.c. (0.01 c.c. of blood) are mixed with 30 c.c. of a 1 per cent. solution of hydrogen peroxide (which, if acid, must first be accurately neutralised since traces of free acid inhibit the reaction), the value of which is ascertained iodimetrically. The reaction is allowed to proceed for 2 hours at 15°, and is then arrested by the addition of 10 c.c. of hydrochloric acid of sp. gr. 1.19. Small variations of temperature do not influence the result materially. Potassium iodide (20—25 c.c. of 10 per cent. solution) is then gradually added, the mixture allowed to remain for 1 hour, and the iodine titrated. The expression "catalase value" is suggested for the number of grams of hydrogen peroxide decomposed by 1 c.c. of blood. In normal blood, this value varies from 18 to 30, but generally lies between 20 and 26. No difference can be observed between the sexes, or between venous and arterial blood, but in various pathological conditions, as tuberculose, nephritis, or carcinoma, a marked diminution is observed. M. J. S.

Apparatus for determining the Differences shown by Tobaccos when Burnt [Smoked]. J. TOTH (*Rev. internat. Falsi.*, 1904, 17, 142—145).—By means of the apparatus described, the author is enabled to numerically express the "combustibility" of a tobacco, that is to say, whether it smokes slowly or quickly as compared with other tobaccos. The tobacco is previously cut as usual, and then made into cigarettes, at least fifteen of the latter being prepared from each sample of tobacco under examination. The cigarettes should be 90 mm. in length and 8 mm. in diameter, and made as nearly as possible of the same compactness. Each lot of cigarettes is dried at 50° and kept in a stoppered bottle. One of the cigarettes is then weighed and fixed by means of an india-rubber tube to a glass tube which passes to the bottom of a Woulff's bottle containing a dilute alcoholic solution of sodium hydroxide. This bottle is connected with a second containing dilute acid, which in turn is connected with a large aspirator filled with water. The exit tube of the aspirator is fitted with a graduated tap. At the moment the cigarette is lighted, the tap is turned on, so that from 45 to 110 grams of water run out per minute, producing a pressure of 2—3 mm. of water on a manometer fixed to a side-tube on the mouth-piece. All water leaving the aspirator is collected and weighed at the end of the experiment, it being assumed that the weight in grams is equivalent to the volume in cubic centimetres of air used. The volume of air multiplied by the time (seconds) of smoking and the result divided by the weight of tobacco (less paper) taken multiplied by 1000 gives a number which is termed the "combustion value" of the tobacco. This value for Turkish tobaccos may range from 400 to 800 or more, but for one sample will not vary more than 15 to 25 if the average of 10 cigarettes is taken. W. P. S.

General and Physical Chemistry.

Spectra of the Fluorides of the Alkaline Earths in the Electric Arc. CHARLES FABRY (*Compt. rend.*, 1905, 140, 578—581).—The band spectra of the fluorides of the alkaline earths (compare Abstr., 1904, ii, 601) are a series of heads of bands and the frequency N of any particular head m is given by the equation $N = A - (Bm + C)^2$, where B and C are constants depending on the origin and direction of numbering, the most brilliant head being called 0, and the succeeding ones 1, 2, 3, &c., in decreasing order of intensity. The values of A , B , and C for corresponding series of calcium and strontium fluorides are given in the original, and the following conclusions are drawn: (1) the constant A is greater in the case of calcium than of strontium, that is, the series is displaced towards the greatest wave-length as the atomic weight of the metal increases; (2) the constant C has the same value for analogous series of the two salts; (3) the constant B diminishes on passing from a calcium series to the analogous series of strontium. In the case of barium fluoride, $B < 0$.

M. A. W.

Emission Spectra of Metals in the Electric Furnace. ARTHUR S. KING (*Ann. Physik*, 1905, [iv], 16, 360—381).—The metals or their salts were placed in an electric furnace similar to that previously used by Liveing and Dewar for the same purpose (see *Proc. Roy. Soc.*, 1882, 34, 119), and raised to a temperature estimated as 2500° abs. The spectra observed are free from the influence of electrical conditions under which arc and spark spectra have been obtained, for the arc used by the author serves only to raise the furnace to a high temperature. The method is especially suited for the production of band spectra. Numerous lines also have been observed, the intensities of which differ markedly from those of the arc spectrum lines. The metals investigated were caesium, calcium, strontium, barium, iron, copper, magnesium, mercury, and zinc. The two last metals, however, gave no lines. For details of the spectra of the other metals, the original must be consulted.

J. C. P.

Relations existing between Constitution and Absorption Spectra of the Thiazines and Thiazones. JULIUS FORMÁNEK (*Zeit. Farb. Text. Chem.*, 1905, 4, 33—38, 61—67).—Measurements are given of the absorption spectra of thionine chloride and of a large number of its methyl and ethyl derivatives in aqueous, ethyl-alcoholic, and amyl-alcoholic solution. Similar considerations to those already brought forward in a previous paper (Abstr., 1904, ii, 106) are developed with regard to the influence of alkyl groups on the displacement of the absorption lines.

W. A. D.

Kehrmann's Explanation of Change of Fluorescence. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1905, 38, 793—794. Compare Abstr., 1903, i, 700; 1904, ii, 528; and Kehrmann, *ibid.*, 797).—The fluorescence of 1:4-dimethoxyacetophenone and α -methylvinylquinol dimethyl ether (this vol., i, 280) cannot be due to the change in position of ortho-quinonoid linkings, as assumed in other cases by Kehrmann. J. J. S.

Present Problems of Radioactivity. ERNEST RUTHERFORD (*Arch. Sci. phys. Nat.*, 1905, [iv], 19, 31—59).—A memoir in which the most important problems connected with radioactivity are discussed, and wherein are indicated the subjects which, in the author's opinion, require further research. Theoretically, the apparent mass of an electron rapidly increases when its velocity approaches that of light, becoming infinitely great when equal to this. Hence it may be concluded that it is not possible for a charged substance to move with a velocity greater than that of light; on this account, a deeper study of the high-speed electrons is desirable. Further researches on the α -rays are also required in order to decide whether the α -particles, which are of the same order of magnitude as the hydrogen atom, are positively charged when expelled, or whether these particles are not charged at the instant of expulsion, but acquire a positive charge by reason of impacts with particles of matter, whereby they lose a negative electron. The apparent non-existence of a positive electron has also to find a satisfactory explanation. The penetrating power of the α -polonium rays is less than that of the α -radium rays, hence probably their velocity is less. This indicates that the value e/m is different for these, and hence the determination of the velocities is important. The curves for calorific effect for the radium transformations agree with those for the activity measured in α -rays, and the question naturally arises whether the bombardment by these particles is sufficient to account for the calorific effect. The number of α -particles emitted per second per gram of radium has been calculated as about 3×10^{11} , that necessary to account for the calorific effect is from 2×10^{11} (Rutherford) to 5×10^{11} (Des Coudres), an accord which is sufficiently close to allow it to be supposed that the heat is solely due to the α -particles, the energy due to β - and γ -rays being small by comparison. Radiation of energy due to rearrangement of the components after the expulsion of the α -particle might be expected, and experiments on this point are desirable. The source of the energy is discussed and the two hypotheses of internal and external sources are considered, the former being regarded as the more satisfactory. The cause of the explosive disintegration of the atom has, however, yet to be explained (compare Abstr., 1904, ii, 223, 799). L. M. J.

Electrical Radiography. V. GABRITSCHESKI (*Chem. Centr.*, 1905, i, 493; from *Physikal. Zeit.*, 6, 33—34).—If a radium preparation and any flat object are brought for a few minutes into the immediate neighbourhood of an electrified ebonite plate, then on dusting the latter with a finely divided mixture of sulphur and red lead, a sharply outlined dust-figure of the object is formed on the ebonite plate.

The object does not need to be in contact with the ebonite plate nor with the radium preparation; if the latter is placed on the opposite side of the plate, the figures make their appearance. The author assumes the existence of a special force which attracts the electrical charge of the plate towards the object in its vicinity.

H. M. D.

Action of Radium Bromide on the Electrical Resistance of Metals. BRONISLAS SABAT (*Compt. rend.*, 1905, 140, 644—646).—The metals (iron, platinum, copper, bismuth) or alloys (brass, German silver) in the form of wires of 0.1 mm. diameter were wound on a paper cylinder and subjected to the action of 0.2 gram of radium bromide contained in a thin glass tube, which was placed in the interior of the cylinder. In all cases, a small increase in the electrical resistance was observed, and this increase was greater than can be attributed to the heating effect of the radium. The total effect is not instantaneous, but a gradual increase to an almost constant maximum is observable.

The observed maximum increase in the resistance of the iron wire examined would correspond with a rise of temperature of 1.6° , whereas the rise of temperature due to the heating effect of the radium is computed to be less than 0.3 — 0.4° . On removing the radium, the resistance sinks slowly to its original value. The author supposes that the metals absorb the β -rays, and that the energy of these rays is transformed into heat energy.

H. M. D.

Ionisation due to Radium Emanation. WILLIAM DUANE (*Compt. rend.*, 1905, 140, 581—583).—The saturation electric current that can be passed across the gas contained in a vessel into which radium emanation is introduced increases rapidly during the first ten minutes, then more slowly, attaining a maximum in about three hours. The initial current is represented by the equation $d = b - k.S/V$, where b is the current that would be produced by unit quantity of emanation if all its radiation were absorbed by the air, and $k.S/V$ is the correction due to the radiation absorbed by the walls of the vessel of surface S and volume V .

M. A. W.

Action of Radium Rays on Mixtures of Hydrogen and Chlorine. WILLIAM P. JORISSEN and WILHELM E. RINGER (*Ber.*, 1905, 38, 899—904).—A summary of the observed cases of chemical action under the influence of radium rays is given. Previous experiments with mixtures of hydrogen and chlorine have given a negative result. The gas mixture was obtained by electrolysis of 25 per cent. hydrochloric acid, and was subjected to the influence of radium bromide in an apparatus resembling a Bunsen ice calorimeter. The radium salt (5 mg.) was placed in the inner thin-walled tube, the gas mixture being contained in the outer larger vessel, into which was sealed a capillary tube, on which any alteration in volume of the gas mixture exposed to the action of the radium was indicated. Disturbances resulting from alteration in the atmospheric pressure were eliminated by a special contrivance. The apparatus was immersed in a thermostat

maintained at 25° and the gas mixture exposed to the radium in the dark. The meniscus of the liquid confining the gas was observed slowly to alter its position in the capillary tube. The same effect was observed when the radium tube was coated with a layer of black varnish in order to cut off the phosphorescent light of the radium. H. M. D.

Molecular Weights of Radium and Thorium Emanations.

WALTER MAKOWER (*Phil. Mag.*, 1905, [vi], 9, 56—77).—The molecular weights of the emanations were determined from comparison of the rate of diffusion with that of gases of known molecular weight, namely, oxygen, carbon dioxide, and sulphur dioxide. Some interesting results were obtained in the preliminary experiments. The diffusion constant with the same plug was found to vary with pressure, a result the author considers to be due to the pores of the plug being comparable in size with the mean free path of gas molecules. The values for hydrogen and carbon dioxide were not in the inverse ratios of the squares of the densities, the result being explicable by differences due to gravitational causes. As the values for $\lambda \sqrt{M}$ were not constant, a curve for $\lambda \sqrt{M}$ against λ was drawn for the known gases, from which from the value of λ for the radium emanation, the value of M is obtained. The results lead to the values 85.5, 97, and 99, so that, if monatomic, it probably occupies the vacancy in the periodic table between Mo = 96 and Ru = 102. The determination of the rate of diffusion of the thorium emanation was rendered more difficult owing to its rapid rate of decay, but full accounts of the methods employed for this and the previous determination are given. The ratio of λ (thorium) to λ (radium) was found to be 1 : 0.931.

L. M. J.

Emanium. FRIEDRICH GIESEL (*Ber.*, 1905, 38, 775—778. Compare Abstr., 1904, ii, 800).—A product much richer in emanium is obtained when the rare earths are carried down with barium sulphate; by this method, considerable amounts of lanthanum are removed. Fractional precipitation with magnesia may also be used for purifying the emanium; this and lanthanum are least readily precipitated.

The active substances which can be separated from emanium by means of ammonia are termed Emanium X or EX, and are also removed by precipitated barium sulphate or other precipitates.

The three lines previously described as characteristic of emanium have been found to be due to didymium—lines λ 590 and 530 to neodymium, and lines λ 530 and 488 to praseodidymium. J. J. S.

Radioactivity of Certain Fresh-water Springs of the Taunus. A. SCHMIDT (*Chem. Centr.*, 1905, i, 492; from *Physikal. Zeit.*, 6, 34—37).—By means of a piston, 600 c.c. of air were forced through 600 c.c. of the water under examination and introduced into a closed cylinder of metal containing an Exner's electroscope. The rate of fall of potential was then measured. Of nine samples which were examined, three were found to be active. The activity is present in the waters in the form of emanation, which is removed by the air forced through them.

In examining a spring-water for radioactivity, the method adopted is to determine the rate of fall of potential in the air forced through the water immediately after the sample has been taken, the measurement being repeated with air forced through the water four days later. If the ratio of the rates of fall of potential is 2 : 1, the authors conclude that the water is radioactive. The fresh-water springs of Wiesbaden are more active than the hot springs, the evolution of gas from the latter removing the emanation. Apart from the emanation, however, the hot springs appear to contain a radioactive element.

H. M. D.

Radioactivity of Mineral Springs. G. A. BLANC (*Phil. Mag.*, 1905, [vi], 9, 148—154).—The author examined the radioactive properties of the deposits from a number of mineral and thermal waters of the Alpine regions, a list of the sources being given. It was found that most produced a certain amount of emanation, the rate of decay of which was approximately equal to that of the radium emanation. Some very active deposits, however, produced very little emanation, or else a very rapidly decaying emanation. Further experiments showed the latter to be present, the emanation losing half its activity in about one minute, and producing secondary activity which decays to half its value in about eleven hours; this is hence probably a thorium emanation.

L. M. J.

The Wiesbaden Thermal Springs and their Radioactivity. FERDINAND HENRICH (*Monatsh.*, 1905, 23, 149—184. Compare this vol., ii, 6; Fresenius, *Abstr.*, 1887, 647).—The gas obtained from the Kochbrunnen, Wiesbaden, was found to consist of 84·5 per cent. of carbon dioxide, including traces of hydrogen sulphide, 0·1 per cent. of oxygen, and 15·4 per cent. of nitrogen and argon; the gas from the Adler spring contained 75·4 per cent. of carbon dioxide with traces of hydrogen sulphide, 1 per cent. of oxygen, and 23·6 per cent. of nitrogen and argon; the gas from the Schützenhof spring contained 63·2 per cent. of carbon dioxide with traces of hydrogen sulphide, 0·2 per cent. of oxygen, and 67·2 per cent. of nitrogen and argon. The composition of the gas from the same spring is not always the same, and the gases from different jets in the same spring basin vary in their composition. The gas from the Kochbrunnen was found to affect a photographic plate. The electrometrical examination of the gases from these three springs showed that in each case the radioactivity of the gas was increased by removal of the carbon dioxide, and to a still greater extent by removal of the nitrogen; the residual gases exhibited the spectrum of argon, but neither of helium nor of radium emanation. The gases obtained by boiling the water of these three springs and of the Faulbrunnen were also found to be radioactive. The solid deposited by the water close to the spring consists principally of ferric oxide and its salts, whilst further from the spring the water deposits calcium carbonate in the form of aragonite; these deposits are strongly radioactive. The residue obtained on evaporation of the water consists principally of sodium chloride, and is only slightly radioactive.

G. Y.

Influence of Temperature on the Electrical Conductivity of Lithium. ARCIERO BERNINI (*Chem. Centr.*, 1905, i, 496; from *Physikal. Zeit.*, 6, 74—78).—The molten lithium was pressed into a glass tube, the walls of which were coated with a thin layer of oil; by this means, the formation of cavities in the solidified metal could be avoided. In the measurement of the electrical conductivity, a correction was applied for this layer of oil. The electrical resistance of lithium alters considerably more than that of sodium and potassium when change in the state of aggregation takes place. From the electrical resistance curves, the melting point of lithium is 177.84° (Bunsen, 180°). The specific resistance of solid lithium at 0° is 0.089285, of molten lithium at 230° , 0.452484. The temperature-coefficient for solid lithium between 0° and its melting point is 0.004568, for molten lithium between the melting point and 230° , 0.002729. In opposition to previous statements, lithium melts quite sharply as indicated by the electrical measurements. The ratio of the specific resistances at the melting point is equal to 2.51.

H. M. D.

Halogen Hydrides as Conducting Solvents. III. Transport Numbers. BERTRAM D. STEELE (*Proc. Roy. Soc.*, 1905, 74, 320. Compare McIntosh and Steele, *Abstr.*, 1904, ii, 533; Archibald and McIntosh, *ibid.*, 534).—As a preliminary step, Faraday's law was shown to be valid for solutions in liquefied hydrogen bromide within the limits of the experimental error of the method employed. Transport numbers were then determined at -81° for ether, acetone, methyl hexyl ketone, and triethylamine hydrobromide in hydrogen bromide solution. These substances, the first two of which have been shown to form compounds with hydrogen bromide, are found to travel towards the cathode, and the cation transport number increases with increasing concentration.

J. C. P.

Halogen Hydrides as Conducting Solvents. IV. BERTRAM D. STEELE, DOUGLAS MCINTOSH, and EBENEZER H. ARCHIBALD (*Proc. Roy. Soc.*, 1905, 74, 321—322. Compare preceding abstract).—To explain the abnormal variation of the molecular conductivity with dilution for solutions in which the halogen hydrides act as solvents (see *Abstr.*, 1904, ii, 534), it may be assumed that the dissolved substance combines with the solvent, and that the resulting compound undergoes ionic dissociation. This view is supported by experiments on solutions of hydrogen cyanide and triethylamine hydrochloride in hydrogen chloride, and of acetone in hydrogen bromide. In the latter case, 3 molecules of solute, in the former cases, 2 molecules of solute, combine with the solvent to form the dissociating substance. The association of solute and solvent in such cases is indicated also by the high values obtained for the molecular weight.

J. C. P.

Electromotive Behaviour of Bromine and the Anodic Potential in the Electrolysis of Neutral Solutions of Potassium Bromide. F. BOERICKE (*Zeit. Elektrochem.*, 1905, 11, 57—88).—The solubility of liquid bromine in water is 0.2595 gram-molecule per litre at 0° and 0.2125 gram-molecule per litre at 25° . Bromine

hydrate is less soluble, the saturated solution containing 0.152 gram-molecule of bromine at 0°.

The following table gives the solubility of bromine and bromine hydrate in solutions of potassium bromide; the concentrations are expressed in gram-molecules of potassium bromide or bromine per litre :

Concentration KBr.	Concentration of Br ₂ .		Concentration of KBr.	Concentration of Br ₂ at 25°.
	Bromine, 0°.	Bromine hydrate, 0°.		
3.033	4.606	—	3.00	3.955
2.17	3.200	3.200	1.00	1.354
1.82	2.650	2.645	0.50	0.744
1.725	2.515	2.475	0.33	0.564
1.00	1.520	1.360	0.20	0.421
0.501	0.8666	0.700	0.10	0.3085
0.330	0.6510	—	0.033	0.2500
0.199	0.4945	0.3575		
0.100	0.3770	0.250		
0.033	0.2935	—		
HBr.			HBr.	
1.00	1.690	1.565	1.00	1.4975
0.10	0.3770	0.262	0.10	0.324

At 0°, bromine, bromine hydrate, and 1.83 normal potassium bromide solution saturated with bromine are in stable equilibrium. The author concludes from the figures given that, whilst the greater part of the dissolved bromine probably exists as KBr₃, molecules of the formula KBr₅, and possibly KBr₇, must also exist.

The potential of bromine, $-\epsilon_0$, is calculated by means of the equation $-\epsilon = -\epsilon_0 + 0.0298 \log C_{\text{Br}_2} / (C_{\text{Br}})^2$ from a large number of determinations of the *E.M.F.* of cells containing a platinum electrode immersed in a saturated solution of bromine in potassium bromide. The concentrations of free bromine and of bromine ions are calculated on the assumption that (in the weaker solutions) only KBr₃ molecules are formed, that KBr₃ and KBr are equally dissociated, and that this dissociation can be calculated from the conductivity. The mean value of $-\epsilon_0$ (referred to the hydrogen electrode) is 1.098 volts.

The result of a very large number of experiments on the potential of the anode in the electrolysis of potassium bromide solutions is that the great solubility of bromine in water or a solution of a bromide allows bromine ions to be discharged reversibly at a platinised platinum anode at potentials lower than the potential of bromine in a saturated solution, whereas at a smooth platinum anode a change takes place in the electrode (probably a layer of gaseous bromine condenses on its surface) which makes it necessary to increase the potential considerably above that of bromine in a saturated solution in order to produce an appreciable current. T. E.

Polarisation observed during Cathodic Liberation of Hydrogen. JULIUS TAFEL (*Zeit. physikal. Chem.*, 1905, 50, 641—712. Compare Abstr., 1900, ii, 588).—In the author's experiments, a

platinum anode was used in all cases, dilute sulphuric acid was the electrolyte, and the cathode consisted of mercury, cadmium, lead, silver, copper, nickel, bismuth, tin, gold, or platinum. The polarisation was determined while electrolysis was proceeding, as evidenced by the distinct liberation of hydrogen. The cathode potential, ϵ , and the cathode current density, I , are related by the equation $\epsilon = a + b \log I$, where a and b are constants for a given temperature (compare Jahn and Schönrock, Abstr., 1895, ii, 178; Jahn, Abstr., 1898, ii, 496; Haber, Abstr., 1900, ii, 257; Russ, Abstr., 1903, ii, 631; Haber and Russ, Abstr., 1904, ii, 309). The potentials for all the metals decrease as the temperature rises, but in the case of mercury it was found that b increases with rising temperature. The foregoing formula is especially accurate for a mercury cathode over a wide range of current density, but its applicability is masked in the case of the other metals (except perhaps lead) by secondary causes. In studying these secondary causes, it is therefore necessary to compare values of the cathode polarisation which have been obtained with a given current density.

The primary influence of the cathode surface, so far as its mechanical properties are concerned, appears to be comparatively slight; for example, polished and prepared lead electrodes have approximately the same polarisation values. But the cathode process itself effects mechanical and chemical changes at the surface of the cathode, and these changes influence the potential values so that the latter are more or less dependent on the previous history of the cathode. Some metals (lead, cadmium, silver, and copper) exhibit two distinct polarisation states when the anode liquid has access to the cathode, a state of "elevation" and a state of "depression." The change from the one to the other takes place during electrolysis, and often occurs suddenly. Cathode process and anode liquid are opposed to each other, and what leads to the state of depression is some change in the cathode surface induced by an unknown product of the anode process.

The potential at all the cathodes (those of platinised platinum and mercury excepted) changes slowly during electrolysis. When the cathode is protected from the anode liquid, lead, cadmium, tin, and bismuth all reach a polarisation maximum within a short time, up to half an hour in the last two cases. With copper, nickel, gold, and bright platinum, the cathode potential for a given current density goes on increasing for hours, and with platinum no maximum value can be reached at all. The author considers that the experimental data are rather opposed to the view of varying polarisation as due to the varying thickness of a gaseous layer on the electrode. He himself regards the cathode surface as having in different cases a different catalytic effect on the process of formation of hydrogen gas. J. C. P.

Relation between Cathode Potential and Electrolytic Reducing Action. JULIUS TAFEL and KURT NAUMANN (*Zeit. physikal. Chem.*, 1905, 50, 713—752. Compare preceding abstract).—The electrolytic reduction of caffeine and succinimide in sulphuric acid can be effected only with cathodes of cadmium, lead, and mercury. In the case of lead, however, the reduction cannot be effected if the cathode potential is by any method reduced below about 1.65 volts. Caffeine

is reduced more rapidly at a mercury cathode than at a lead cathode, but the behaviour of succinimide is exactly the reverse, although the cathode potentials of the two metals in pure acid are the same. In the electrolysis of sulphuric acid with mercury cathode, the addition of caffeine leads to depolarisation. With a lead cathode, small quantities of caffeine effect a rise of the cathode potential, larger quantities lower the potential. Succinimide raises the potential at both mercury and lead cathodes. Addition of caffeine at a tin cathode leads to depolarisation, although no reduction of the caffeine can be detected. When caffeine is reduced at a mercury cathode, then for a given current strength the relation $\epsilon = a + b \log(100 - N)$ holds, where ϵ is the cathode potential during the reduction and N is the reduction efficiency ("Nutz-effekt"). When caffeine is reduced at a lead cathode, the potential of which in pure acid is varied by the precipitation of foreign metals, then for a given current strength and caffeine concentration the relation $\epsilon = a_1 + b_1 \log N$ holds. These results are in harmony with the observations of Haber and his pupils on the reduction of nitrobenzene without evolution of hydrogen. They can be interpreted by supposing that the formation of hydrogen gas and the reduction at the cathode are completely co-ordinated non-reversible processes, and that the cathode potential is due to the forced accumulation of hydrogen in some form or other in the surface layer of the cathode. J. C. P.

Theory of Electrocapillary Phenomena. III. JEAN BILLITZER (*Zeit. physikal. Chem.*, 1905, 51, 167—192).—Recent work has shown that the capillary constant of mercury not only depends on the density of the electrical double layer, but is a function also of the potential difference. In the present paper, the author deduces and discusses a form of this function. J. C. P.

The Aluminium Rectifier. S. BARCLAY CHARTERS (*J. Physical Chem.*, 1905, 9, 110—148).—The behaviour of an aluminium rectifier is best explained by the assumption that the electrode becomes coated with a film of aluminium hydroxide which is impermeable to certain ions, for example, SO_4'' and Al''' , but permeable to others, such as H^+ , Cl^+ , Br^+ (*Abstr.*, 1903, ii, 260). When a low voltage is applied and slowly increased with clean aluminium electrodes, a considerable current is first produced, which gradually sinks as the film increases, until a steady low value is reached—the leakage current, which increases slowly with the voltage until a certain critical value of the voltage is obtained above which the current increases rapidly, the film being ultimately ruptured at what is termed the "break-down point." Experiments were first made to determine the critical values with various electrolytes, and the method employed is described, tables and curves of the results being given. Sulphuric acid and solutions of disodium phosphate and citric acid were employed; the critical value of sulphuric acid was lowest, about 55 volts, that of dilute citric acid was highest, but in this case, owing to steady rise of the leakage current, the solution cannot be worked above about 325 volts. The other two solutions yielded a critical value of about 300 volts, the same value being obtained with phosphoric acid at a concentration of maximum

conductivity, and this solution was employed in the 4-cell rectifier described. The rectifier was arranged to secure all the current, and lead graphite was employed as the second electrode. Numerous experiments on the efficiency of the rectifier were made, and curves are given. A current efficiency of about 75—80 per cent. was readily obtained; the voltage efficiency, however, is only about 30 to 35 per cent., and the energy efficiency about 20 to 30 per cent. The loss of voltage is best explained by assumption of a counter *E.M.F.*

L. M. J.

Behaviour of Anodes of Iridium, Platinum, and Rhodium in the Electrolysis of Dilute Sulphuric Acid. J. B. WESTHAVER (*Zeit. physikal. Chem.*, 1905, 51, 65—94).—Anodes of iridium, platinum, and rhodium in *N*/10 sulphuric acid behave differently. When the current density is high, iridium is the least polarisable, followed by rhodium; at low values of the current density, platinum is less easily polarised than iridium. A considerable interval elapses before the stationary condition of affairs is reached; at low current densities, the most rapid electrodes in this respect are those obtained by covering a glass surface with a liquid containing iridium salt, and then evaporating and igniting. With such burnt electrodes, coated with iridium black, the *E.M.F.* of the hydrogen-oxygen cell with *N*/10 sulphuric acid is found to be 1.06 volts at the ordinary temperature, this final value being reached both from above and from below. With platinised electrodes a temporary rise of the *E.M.F.* to 1.1 volts is observed. Oxygen electrodes completely immersed in the liquid exhibit an *E.M.F.* of only 0.9 volt, even after prolonged passage of oxygen. The curves showing the relation between potential and current density exhibit marked hysteresis in the case of platinum and platinum black. The mere occurrence of discontinuities or points of marked curvature on the potential current curves is not sufficient to warrant conclusions as to the electrode processes, for the electrode potentials corresponding with these points depend on the scale of the curves and the accuracy of the method used to determine the current. The author shows that when the logarithm of the current is plotted against the electrode potential, curves are obtained for the various kinds of platinum and iridium electrodes, which all exhibit a break at 1.45 volts. Electrodes of iridium black, on account of their small polarisation, are suitable for determinations of conductivity with alternating current and a telephone.

J. C. P.

Dissociation of Ternary Electrolytes. GOTTFRIED KÜMMEL (*Zeit. Elektrochem.*, 1905, 11, 94—99).—The author has extended the work previously described (*Abstr.*, 1904, ii, 111). Solutions of magnesium chloride are examined at six temperatures between 15° and 30°. The concentrations of the MgCl^+ ions calculated by means of the transference numbers are often smaller than the minimum values calculated by the method of isohydric solutions. This discrepancy is attributed to the inaccuracy of two assumptions on which the calculations are based; these assumptions are: (*a*) the concentration of the Cl^- ions in a solution of potassium chloride can be calculated from its conductivity;

(b) the transference numbers are independent of the concentration. On the whole, however, it appears that the concentration of the MgCl' ions increases rapidly as the temperature rises. Similar experiments are described with calcium chloride and nitrate, barium chloride, potassium oxalate, and lithium sulphate. The results obtained with the calcium and barium salts are very similar to those obtained with magnesium chloride; potassium oxalate also gives similar results. The transference number for K in potassium oxalate is found to be 0.76 in 2*N*- and 0.74 in *N*-solutions at 25°. The transference number for Li in LiSO_4 at 25° is found to be 0.35 in 2*N*-, 0.37 in *N*-, and 0.39 in 0.5*N*-solutions. The values of the concentrations of the ion LiSO_4' found by the two methods agree much better in this case than in any other; at 25° they are:

Litres per gram equivalent Li_2SO_4 ...	0.5	0.571	0.667	1	2	10
Concentration of Li' ions	0.930	0.847	0.752	0.546	0.303	0.0692
Concentration of LiSO_4' ions. {	Maximum	0.930	0.789	0.654	0.404	0.157
	Minimum	0.530	0.454	0.376	0.233	0.090
	From transference number	0.717	0.597	0.499	0.301	0.106
					0.106	0.0028

T. E.

Electrolysis with Alternating Current. ANDRÉ BROCHET and JOSEPH PETIT (*Zeit. Elektrochem.*, 1905, 11, 102).—Reply to Le Blanc (this vol., 137) and Ruer (*ibid.*). T. E.

Electrolysis of Organic Acids by means of an Alternating Current. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1905, 140, 442—444. Compare this vol., ii, 7, 27, 28).—Solutions of formic acid, formates, or oxalic acid are electrolytically decomposed by means of an alternating current, yielding the same products as are obtained when a continuous current is employed, but the yields, which vary with the current density, are much higher; in the case of formic acid with a current density of one ampere per sq. centimetre, the yield is 46 per cent. of the theoretical, with 0.5 ampere it is 10—12 per cent., and with 0.25 ampere it is 5 per cent.; the corresponding values for potassium formate are 80—90 per cent., 30—40 per cent., and 10—15 per cent., whilst the yield of gaseous products from oxalic acid is 80 per cent. for a current density of 1 ampere per sq. centimetre. The alternating current has no definite action on acetic acid solutions.

M. A. W.

Registration of Atmospheric Ionisation by means of Falling Water. CHARLES NORDMANN (*Compt. rend.*, 1905, 140, 430—433).—A description and diagram of an arrangement for obtaining a continuous record of the ionisation of the atmosphere (compare *Compt. rend.*, 1904, 138, 1418, 1596); the air circulates between the plates of a cylindrical condenser and the charge introduced by the ions is carried off by drops of water falling regularly from a Mariotte bottle; the deviations of the electrometer connected with the condenser are proportional to the number of ions per unit volume of the gas, and a photographic record of the deviations is obtained on a mechanically rotating cylinder.

M. A. W.

Magnetic Hysteresis at High Frequencies. CH. EUG. GUYE and A. SCHIDLOF (*Arch. Sci. phys. Nat.*, 1905, [iv], 19, 60—79).—The authors have compared by a bolometric method the energy lost per second by hysteresis in coils of iron, nickel, and nickel steel in fields of varying intensity and at frequencies varying from 125 to 1200. It is found that the energy lost per second is proportional to the frequency, and hence that the energy lost in each cycle of magnetism is independent of the time of the cycle within the limits of 100 to 1200 cycles per second. L. M. J.

Magnetisation and Resistance of Nickel Wire at High Temperatures. C. G. KNOTT (*Trans. Roy. Soc. Edin.*, 1904, 41, 39—52).—The experiments deal with the effect of longitudinal magnetisation on the electrical resistance of nickel wire up to 400°, the temperature about which nickel loses its pronounced magnetic properties. The results are summarised in two sets of graphs, namely, (1) isothermals, showing the relation between magnetising force and resistance change at various temperatures, and (2) isodynamics, showing the relation between resistance change and temperature in the various fields. In the higher fields, the resistance change diminishes as the temperature rises and is practically non-existent above 350°. Hence it appears that the change in question is a function not of the magnetising force but of the magnetisation or induction in the nickel. The isodynamic curves further indicate a peculiarity at or near 180°. This is probably connected with the abnormal thermoelectric behaviour of nickel at 180—200°, and with the abnormal temperature-coefficient of the resistance of nickel at the same temperature. J. C. P.

Coefficient of Magnetisation of Bismuth: Some Points of Reference in the Diamagnetic Scale. GEORGES MESLIN (*Compt. rend.*, 1905, 140, 499—502).—The author has redetermined the value of the coefficient of magnetisation of crystalline bismuth and finds -1.42×10^{-6} ; Faraday found -1.64×10^{-6} ; Becquerel, -1.75×10^{-6} ; Curie, -1.35×10^{-6} ; and Ettingshausen, -1.44×10^{-6} . For potassium sulphate or nitrate, the value of the coefficient is -0.42×10^{-6} or 0.32×10^{-6} respectively, and these agree closely with the values found by Curie, namely, -0.43×10^{-6} for potassium sulphate and -0.33×10^{-6} for potassium nitrate. M. A. W.

Specific Heat of Gases at High Temperatures. LUDWIG HOLBORN and L. AUSTIN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 175—178).—The mean specific heats at constant pressure of nitrogen, air, oxygen containing 9.5 per cent. of nitrogen, and carbon dioxide have been determined by Regnault's method over the temperature ranges 20—440°, 20—630°, 20—800°. From the specific heat of the impure oxygen just referred to, the specific heat of pure oxygen has been calculated. The values found for the mean specific heats are given in the following table:

Temp. range.	Nitrogen.	Oxygen.	Air.	Carbon dioxide.
20—440°	0.2419	0.2240	0.2366	0.2306
20—630	0.2464	0.2300	0.2429	0.2423
20—800	0.2497	—	0.2430	0.2486

It is not possible from these results to say with certainty that the specific heat of the simple gases increases with rising temperature. When the specific heat of carbon dioxide at a definite temperature is calculated from the mean specific heats, the following numbers are obtained :

Temperature.	Specific heat.	Temperature.	Specific heat.
0°	0·2028	400°	0·2502
100	0·2161	600	0·2678
200	0·2285	800	0·2815

The values at the higher temperatures are lower than those deduced indirectly by previous workers. J. C. P.

Effect of Liquid Air Temperatures on the Mechanical and other Properties of Iron and its Alloys. SIR JAMES DEWAR and ROBERT A. HADFIELD (*Proc. Roy. Soc.*, 1905, **74**, 326—336).—The effect of low temperature on iron and iron alloys is, in general, to increase their tenacity and reduce their ductility. This does not apply, however, to the alloys containing nickel. Whereas pure iron becomes extraordinarily brittle at low temperatures, the effect of these conditions on nickel is to increase both its tenacity and its ductility, and the influence of the latter characteristic may be marked in the iron-nickel alloys. The nickel, in fact, acts as a preventive of brittleness at low temperatures, provided the percentage of carbon in the alloy is not too great. Even in an iron alloy containing 6 per cent. of manganese and 24 per cent. of nickel, the latter metal causes the alloy to remain ductile at the temperature of liquid air. J. C. P.

Melting Points and Transition Points* of some Salts. K. HÜTTNER and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, **43**, 215—227).—In determinations of the melting points of salts, the curves of cooling over as large a temperature range as possible should be observed in order that the transition points of one crystalline form into another may be noted. The curve of cooling also indicates the relationship between the heat of transition and the heat of fusion. The transition proceeds in such a manner that the amount of substance which crystallises in unit of time gives up an amount of heat which is just sufficient to maintain the temperature constant for a time. The amount of salt transformed in unit of time depends on the temperature, on the linear rate of crystallisation with which the single crystals separate in the molten mass, and on the nature of the distribution of the crystals in the molten mass.

The curve of cooling of lithium sulphate is represented, the ordinates indicating temperatures and the abscissæ time in seconds. From observations of temperature during the crystallisation of the first half of the salt, conclusions can be drawn as to whether any substance is present in admixture with the salt.

The relationship between heat of transition and heat of fusion is discussed. The latter is always greater than the former for any given salt.

The melting and transition points of a number of inorganic salts

were determined. Many of the melting points determined by the authors are widely at variance with values previously obtained by Braun, Carnelley, Le Chatelier, and others.

A. McK.

Vapour Tension of Solid Solutions. II. ALEXANDER W. SPERANSKY (*Zeit. physikal. Chem.*, 1905, 51, 45—58. Compare Abstr., 1904, ii, 237).—With the apparatus previously described, the author has determined the vapour tensions at various temperatures of *p*-dibromobenzene (solid), *p*-chlorobromobenzene (m. p. 64·7°; solid and liquid), *p*-dichlorobenzene (solid and liquid), and of isomorphous mixtures of *p*-dibromobenzene with *p*-chlorobromobenzene, and of *p*-dibromobenzene with *p*-dichlorobenzene. From the vapour pressure curves for solid and liquid *p*-dichlorobenzene and *p*-chlorobromobenzene, it is possible to calculate the freezing point (that is, the intersection of the curves) in good agreement with experiment. From the vapour tensions of the isomorphous mixtures, it appears that in a solid solution of *p*-dibromobenzene in *p*-chlorobromobenzene the molecules of the former substance are simple, while in a solid solution of *p*-dibromobenzene in *p*-dichlorobenzene the molecules of the former substance at high concentrations are double. The result is the same as has been deduced from the study of the liquid solutions. Since the solution laws are thus applicable in the case of these isomorphous mixtures, it may be concluded that the surface of the solid does not play an important part.

J. C. P.

Determination of Molecular Weight in Solid Solutions.
IV. Vaporisation of Isomorphous Mixtures of *p*-Dichlorobenzene and *p*-Dibromobenzene. FRIEDRICH W. KÜSTER [with GEORG DAHMER] (*Zeit. physikal. Chem.*, 1905, 51, 222—242. Compare this vol., ii, 80; also Speransky, preceding abstract).—An elaborate apparatus has been devised for determining the vapour pressures of *p*-dichlorobenzene, *p*-dibromobenzene, and isomorphous mixtures of the two substances. The vaporisation took place in a large bell jar immersed in a thermostat, and provision was made for the stirring of the vaporising substance and for the circulation of the air and vapour in the bell jar. When the air in the bell jar had become saturated with the vaporising substance, it was aspirated over a column of hot lime. The amount of halogen in the lime was subsequently determined by Volhard's method. The vapour pressure of the bromine compound has been determined at various temperatures between 19·3° and 69·1°, the vapour pressures of the chlorine compound and of the isomorphous mixtures at 49·1°, at which temperature the vapour pressures of *p*-dichlorobenzene and *p*-dibromobenzene are 5·23 and 0·31 mm. mercury respectively. The curve exhibiting the variation of vapour pressure of the isomorphous mixtures with their composition does not deviate much from a straight line, although the mixtures with 0—60 per cent. chlorobenzene have a slightly greater vapour pressure, those with 60—100 per cent. chlorobenzene a slightly lower vapour pressure than that given by the straight line. The partial pressure curve for the chlorobenzene is regular, but that for the bromobenzene is peculiar, in that the vapour pressure of the bromobenzene in mixtures containing 57—100 per cent. of that compound is greater than that of the

pure bromobenzene. Mixtures of any composition between those limits should therefore separate gradually into pure dibromobenzene and the mixture with 57 per cent. This is a case of supersaturated solid solutions (compare Abstr., 1895, ii, 439), and these results are not in harmony with the earlier work (Küster and Würfel, this vol., ii, 80). Accordingly, fresh experiments have been made on the solubility of the isomorphous mixtures in aqueous alcohol at 49.1° , and it is found that the solubility of *p*-dibromobenzene from a 59 per cent. mixture is as great as that of the pure bromine compound itself, whilst the solubility of *p*-dibromobenzene from mixtures containing 80–90 per cent. of that compound is greater than that of the pure dibromobenzene. The consequent separation of a 92.5 per cent. mixture into pure *p*-dibromobenzene and the mixture with 57 per cent. of the bromine compound has been directly observed, at least in its initial stages.

J. C. P.

Boiling Points of Homologous Compounds. SYDNEY YOUNG (*Phil. Mag.*, 1905, [vi], 9, 1–19).—Since the time of Kopp, various expressions have been proposed for the boiling points of homologous series, notably (1) the formula $T = aM^b$ due to Walker, in which T is the absolute boiling point, M the molecular weight, and a and b are constants; (2) that due to Ramage, $T = a[M(1 - 2^{-u})]^{\frac{1}{2}}$, where u is the number of carbon atoms in the molecule. The author considers that the rise of boiling point for an increment of CH_2 may be usefully regarded as being mainly a function of the absolute temperature, and adopts provisionally the formula $\Delta = 144.86/T^{0.0148\sqrt{T}}$, which was derived for the homologous paraffins. It is shown that for these compounds the agreement between calculated and observed values is better than that obtained by Ramage's formula. The formula was applied also to halogen compounds, ethers, amines, aldehydes, esters, alcohols, acids, cyanides, ketones, and nitro-compounds, care being taken only to accept the values for the boiling points for which accuracy could be expected. From the data as a whole, he considers the formula gives errors rarely exceeding 1.5° , and generally less than 1° if the compounds contain one or more $\text{C}-\text{CH}_2-\text{C}$ groups and are not associated. The accord is better for iso-compounds than for normal, and holds fairly well in associated compounds if their molecular weight is sufficiently high. The values are too high for associated compounds and for the lowest members of the series (*Trans.*, 1903, 83, 68).

L. M. J.

Theory of the Heat of Combustion and the Heat of Formation of Hydrocarbons in the Gaseous State. JULIUS THOMSON (*J. pr. Chem.*, 1905, [ii], 71, 164–181).—A reply to Lagerlöf (*Abstr.*, 1904, ii, 382, 605; this vol., ii, 76).

G. Y.

Certain Heats of Dilution. JOSEPH E. TREVOR (*J. Physical Chem.*, 1905, 9, 90–109).—A mathematical paper in which the author investigates by the method of the thermodynamic potential the heats of irreversible dilution of a two component one phase system.

L. M. J.

Pycnometer for Small Quantities (0.1—0.5 gram) of Solid Substances. JULES JACOBSEN (*Chem. Centr.*, 1905, i, 489; from *Bull. Soc. chim. Belg.*, 1904, 18, 198—200).—The pycnometer has the form of a small bottle of 2—3 c.c. capacity, and is provided with two necks. One of these, 12 cm. long and 1—1.5 mm. in diameter, is divided into 100 parts of a total volume of 0.1 c.c. The second neck, about 5 mm. in diameter, is provided at its extremity with a copper tube, through which a well-fitting screw-stopper works; by means of this, the level of the liquid in the wider neck is always brought to a definite point.

The apparatus is filled with a suitable liquid and the level read off in the capillary neck; a weighed quantity of the substance is then introduced through the wider tube, and after adjustment of the end of the liquid column to the mark by means of the screw stopper, the level in the capillary is again read off. The difference in the two readings represents the volume of the solid substance introduced (compare MacKenna, *Abstr.*, 1899, ii, 467). H. M. D.

Density Determinations with a Pipette. Adjustment of Titrimetric Solutions by Volume Weight. FRIEDRICH W. KÜSTER and SIEGMAR MÜNCH (*Zeit. anorg. Chem.*, 1905, 43, 373—383).—The estimation of the weight of a given volume of an aqueous solution by means of a float of 10 c.c. is accurate to the extent of at least ± 0.0001 without any special precautions being taken and where only one determination is made. The same extent of accuracy may be attained by comparison of the weights of water and of solution respectively which an ordinary 100 c.c. pipette delivers at a given temperature. The accuracy of the measurement of volume by a 100 c.c. pipette may be ± 0.00005 , if the neck of the pipette be chosen sufficiently narrow.

Density determinations with a pipette are sufficient for the preparation of normal solutions. Figures are quoted where the accuracy of the method is indicated in the case of the preparation of standard solutions of hydrochloric acid. A. McK.

Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure. LORD RAYLEIGH (*Proc. Roy. Soc.*, 1905, 74, 446. Compare *Abstr.*, 1903, ii, 313).—The quotient of the value of pv at half an atmosphere by the value at one atmosphere is given for various gases at specified temperatures. The numbers differ slightly from those given in the preliminary communication.

	Oxygen.	Hydrogen.	Nitrogen.	Carbon monoxide.	Air.	Carbon dioxide.	Nitrous oxide.
Temp. ...	11.2°	10.7°	14.9°	13.8°	11.4°	15.0°	11.0°
	1.00038	0.99974	1.00015	1.00026	1.00023	1.00279	1.00327

The compressibilities at 0° are calculated, and from these the ratios of the densities as they would be observed at 0° and under very low pressures are deduced.

From the densities of oxygen and nitrogen, the atomic weight of nitrogen = 14.008 (O = 16). From the densities of oxygen and nitrous oxide, N = 13.998. H. M. D.

Surface Tensions of some Organic Liquids. JULES BOLLE and PHILIPPE A. GUYE (*J. Chim. phys.*, 1905, 38—49).—The values for the surface tension contained in the paper were obtained in the course of experiments on the weights of drops and the surface tension (Abstr., 1901, ii, 374). The temperatures range from the ordinary temperature to about 150°, and the compounds for which the values are given are phenol, *o*-cresol, *m*-cresol, quinoline, butylthiocarbimide, and phenylthiocarbimide. The results indicate association in quinoline at the lower temperatures, whilst abnormal changes of complexity with temperature were observed in the case of *m*-cresol. During the course of the work, a number of densities at various temperatures were determined, the compounds being cymene, amyl acetate, ethyl oxalate, *o*-cresol, *m*-cresol, benzophenone, anethole, methylpropylketoxime, quinoline, butylthiocarbimide, and phenylthiocarbimide.

L. M. J.

Diffusion of Hydrogen through Palladium. OWEN W. RICHARDSON (*Proc. Camb. Phil. Soc.*, 1905, 13, 27—32).—The experimental data obtained by Schmidt (Abstr., 1904, ii, 312) for the rate of diffusion of hydrogen through palladium, are applied to the author's formula for the rate of diffusion with the view of testing whether the diffusion takes place through the metal by means of hydrogen atoms or whether the assumption of molecular dissociation into atoms of hydrogen is unnecessary. The calculated results are not decisive, and the author shows that the differences of pressure employed in the diffusion experiments are not large enough to settle the question. On the assumption of dissociation and by making use of the temperature variation of the rate of diffusion, the heat absorbed in the dissociation of one gram-molecule of hydrogen within the metal is calculated to be 10.88×10^{-3} cal. More accurate experiments are required before the question of the condition of the diffusing hydrogen can be definitely settled.

H. M. D.

Rôle of Diffusion during Catalysis by Colloidal Metals and Similar Substances. HENRY J. S. SAND (*Proc. Roy. Soc.*, 1905, 74, 356—369).—A critical discussion of Nernst's theory of reaction velocity in heterogeneous systems (see Nernst, Abstr., 1904, ii, 315; also Bodenstein, *ibid.*, 245; Brunner, *ibid.*, 315) in the light of the experimental data supplied by Bredig and others (see Bredig and von Berneck, Abstr., 1900, ii, 213; Bredig and Ikeda, Abstr., 1901, ii, 441; Bredig and Reinders, *ibid.*, 442; Senter, this vol., i, 107). The author contends that the variation of the reaction velocity (1) with the concentration of the catalyser, (2) with the temperature, cannot be reconciled with Nernst's conception of a heterogeneous reaction unless the part played by convection is taken into account. On the basis of Nernst's hypothesis, a formula is deduced for the reaction velocity corresponding with a minimum amount of convection, and it is shown that the velocity constant thus calculated is greater than the experimental values found by Bredig, whereas the reverse ought to be the case. In other words, Bredig's reaction proceeds far too slowly to be reconciled with Nernst's hypothesis. If, however, the assumption that

equilibrium is permanently maintained on the boundary between the particles and the solution is abandoned, and it is assumed instead that the reaction velocity at the surface of the particles is proportional to the concentration of the solution in immediate contact with them, it is possible to deduce a formula which corresponds with the experimentally determined course of the reaction. J. C. P.

Some Phenomena which can occur in the case of Partial Miscibility of Two Liquids, one of them being Anomalous, Especially Water. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 517—531).—A theoretical paper. J. C. P.

Contribution to the Theory of Solution. GEOFFREY MARTIN (*J. Physical Chem.*, 1905, 9, 149—155).—As the molecules of a liquid are in motion, the sphere of molecular activity may be taken as the distance beyond which one molecule does not cause appreciable curvature of the path of a second molecule. Owing to increase of velocity, this decreases with temperature, inasmuch as the force one molecule must exert on the other is increased. If a molecule of a second substance is present in solution, then, if the attraction of the liquid molecules on each other is greater than on this, the liquid will be drawn away from around it and it will possess greater freedom of movement. If, on the contrary, this attraction is less, the molecule will unite with liquid molecules until a new molecule is formed for which the previous case obtains. Owing to the same drawing away of the water molecules from around the solute molecules, if the distance between the latter is sufficiently small, they will draw together and separate from the solution, that is, solubility is limited, but increases with temperature. Miscibility of two liquids is due to equality of the attractive forces, and the dissociation of many substances in solution is explained by the reduction of the pressure around the molecule as seen above. L. M. J.

Concentrated Solutions. JOHANNES J. VAN LAAR (*Chem. Centr.*, 1905, i, 491; from *Chem. Weekblad*, 2, 1—16).—The author gives a warning against the danger of carrying the analogy between gases and dilute solutions too far. He considers that the osmotic pressure in the case of an isolated solution is purely a mathematical fiction. For the theoretical treatment of concentrated solutions, the introduction of osmotic pressure correction terms analogous to van der Waals' gas correction factors is not practicable; it is, however, possible to subject such solutions to mathematical treatment by making use of the conception of thermodynamic potential.

The conclusion drawn by Jones and Getman that the deviations from van't Hoff's theory of solutions exhibited by concentrated aqueous solutions are due to the formation of hydrates is severely criticised. H. M. D.

Phenomena Observed when the Plait Curve meets the Solubility Curve. ANDREAS SMITS (*Zeit. physikal. Chem.*, 1905, 51, 193—221).—Largely theoretical. The experimental work

recorded in the paper has been already described (see Abstr., 1904, ii, 15).
J. C. P.

Rate of Solution of Zinc. ERICH BRUNNER (*Zeit. physikal. Chem.*, 1905, 51, 95—105. Compare Abstr., 1904, ii, 315; also Ericson-Aurén and Palu-aer, Abstr., 1902, ii, 64; 1903, ii, 718).—Zinc containing lead as impurity dissolves too slowly in hydrochloric acid to admit of the view that the acid is always exhausted at the surface of the metal. When pure electrolytic zinc dissolves in an iodine solution, the iodine concentration is practically zero at the surface of the metal, that is, the velocity of solution is determined by the rate of diffusion of the iodine; when the zinc contains lead as impurity, the rate of solution is lower, and falls off rapidly with the time. The author has studied also the rate of anodic solution of zinc in a millinormal solution of zinc salt, and finds that the concentration of the zinc ions at the anode is related to the polarisation in accordance with Nernst's formula; when, however, the zinc salt solution is stronger (up to centinormal), the concentration of the zinc ions is smaller than the formula requires. It has not been found possible to give a theory which interprets all the three solution processes referred to above.

J. C. P.

Proof of the Formation of Complexes between Acids with the Help of the Laws of Isohydric Solutions. ROBERT HOFMANN (*Zeit. physikal. Chem.*, 1905, 51, 59—64. Compare Abstr., 1904, ii, 10).—Iodic and sulphuric acids obey the laws of isohydric solutions exactly, and therefore do not form complexes in aqueous solution. Evidence, however, has been obtained of the formation of complexes between iodic and chromic acids, and also, although less definitely, between (1) sulphuric and phosphoric acids, and (2) hydrobromic and phosphoric acids.

J. C. P.

Formation of Salts in Solution, especially in the Case of Substances Exhibiting Tautomerism (Pseudo-acids, Pseudo-bases). II. JULIUS W. BRÜHL and HEINRICH SCHRÖDER (*Zeit. physikal. Chem.*, 1905, 51, 1—18. Compare Abstr., 1904, i, 646, 969; this vol., ii, 70).—Ethyl acetoacetate has been mixed with the equivalent quantity of sodium ethoxide in alcoholic solution, and the spectrochemical constants of the various constituents have been determined before and after mixture. The comparison of these, with the aid of Biot and Arago's mixture law, shows that immediate and complete enolisation takes place on mixing. Further, the alteration of the spectrochemical constants, which is the evidence of enolisation, cannot be attributed to the formation merely of any additive compound of the ester and the sodium ethoxide.

J. C. P.

Condition of a Chemical Reaction forming a Monovariant System. CAMILLE MATIGNON (*Compt. rend.*, 1905, 140, 512—515).—A monovariant system of $n + n' - 1$ components, one gaseous, the rest solid, is capable of forming a reversible reaction if $Q > L + S$, where Q is the heat developed during the direct reaction at the temperature T when the dissociation pressure is 760 mm. and L and S

the molecular heats of fusion and volatilisation respectively of the gaseous substance. Thus, the reaction $2\text{BaO sol.} + \text{O}_2 \text{ gas} \rightleftharpoons 2\text{BaO}_2 \text{ sol.} + 24.1 \text{ Cal.}$ is reversible at 480° , because for oxygen $L + S = 2.7 \text{ Cal.}$, and the temperature at which the dissociation pressure is 760 mm. is $24100/32 = 753^\circ \text{ abs. or } 480^\circ \text{ C.}$; similarly, the reaction $\text{Na}_2\text{SO}_4 \text{ sol.} + \text{HCl gas} \rightleftharpoons \text{NaHSO}_4 \text{ sol.} + \text{NaCl sol.} + 16.9 \text{ Cal.}$ is reversible at 255° , because for HCl $L + S = 5.7 \text{ Cal.}$, and the temperature at which the dissociation pressure is atmospheric is $16900/30 = 528^\circ \text{ abs. or } 255^\circ \text{ C.}$

M. A. W.

Cause of the Period of Chemical Induction in the Union of Hydrogen and Chlorine. DAVID L. CHAPMAN and CHARLES H. BURGESS (*Proc. Roy. Soc.*, 1905, **74**, 400. Compare Bevan, *Abstr.*, 1904, ii, 21; 1902, ii, 237; Mellor, *Trans.*, 1902, **82**, 1280 and 1292; 1901, **79**, 216).—The view that the period of induction is due to the preliminary formation of an unstable intermediate compound is not in accord with the experimental observations recorded by the authors. The phenomenon is due to the presence in the gas (or in the aqueous solution in contact with it) of substances capable of reacting with chlorine. The retardation of chemical action does not depend on the condition of the hydrogen. Water and aqueous solutions possess the power of rendering active chlorine inactive towards hydrogen. On long contact with chlorine in the presence of light or on boiling with chlorine, these solutions lose this property. The only way in which the solutions recover the power of rendering active chlorine inactive is by the introduction of substances which react with chlorine. Of such substances, ammonia is very effective even in minute quantities, and sulphur dioxide acts in a similar way. An active mixture of hydrogen and chlorine does not become inactive when kept for several hours in the dark. Such a mixture, after keeping for several days in the dark, showed no signs of an induction period.

H. M. D.

Union of Hydrogen and Oxygen at Low Pressures through the Passage of Electricity. P. J. KIRKBY (*Phil. Mag.*, 1905, [vi], **9**, 171—185).—The author has previously shown that when a luminous discharge passes through hydrogen and oxygen in equivalent proportions at low pressures, partial union occurs (*Phil. Mag.*, Feb. 1904). If Δp mm. is fall of pressure associated with the passage of ΔQ coulombs at pressure p mm. and potential difference X , then $1/p \cdot \Delta p / \Delta Q$ is a function of X/p . The experiments are continued, and it is seen that $\Delta p / \Delta Q$ is independent of the distance between the plates and that the function is approximately linear, the curve being a straight line, $\Delta p / p \cdot D \cdot \Delta Q = 1/10 + 3X/800pD$, where D is the distance between the plates. If W is the number of molecules of water vapour connected with the passage to the electrode of each pair of ions, it is shown that $W = 4\Delta p / \Delta Q$, and hence $W = 4(pD/100 + 3X/800)$, and the probable physical interpretation of this result is given.

L. M. J.

Reaction Velocity and Free Energy. ERICH BRUNNER (*Zeit. physikal. Chem.*, 1905, **51**, 106—107).—There is no ground for supposing that, if it were possible to remove entirely the products of a reaction in a homogeneous system, the initial velocity of such a reaction would be infinitely great.

J. C. P.

Decomposition of Ammonium Nitrite. ARTHUR A. BLANCHARD (*Zeit. physikal. Chem.*, 1905, **51**, 117—122. Compare Abstr., 1903, ii, 18).—A reply to Arndt's criticism (Abstr., 1904, ii, 16).

J. C. P.

Velocity of Change in Catalytic Reactions. CARL KULLGREN (*Zeit. physikal. Chem.*, 1905, **51**, 108—116).—A reply to Euler's criticism (Abstr., 1904, ii, 318) of the author's work (Abstr., 1903, ii, 535).

J. C. P.

The System Pyridine and Methyl Iodide. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 468—470).—Pyridine methiodide is rapidly formed at temperatures higher than 60° from mixtures of pyridine and methyl iodide. The formation of pyridine methiodide at low temperatures has been examined; the results are represented by curves. The solid compound exists in a metastable form. It is shown that the two liquids, pyridine and methyl iodide, which are miscible in all proportions, may yield two sets of co-existing liquids owing to the formation of a chemical compound. The sharp intersection of the melting point lines at 117° and the elevation of the boiling point after the combination, pyridine boiling at 116°, methyl iodide at 42°, and the mixture at 270°, show that even in the liquid state the compound is certainly for the greater part undissociated.

A. McK.

Action of Enzymes, Toxins, Antitoxins, and Agglutinins. VICTOR HENRI (*Zeit. physikal. Chem.*, 1905, **51**, 19—32).—An unfavourable criticism of the work of Barendrecht (Abstr., 1904, ii, 551, 719), Herzog (Abstr., 1904, ii, 164, 506), and Visser. The author outlines the basis on which he considers any theory of enzyme action must be founded. Solutions of enzymes, toxins, &c., are regarded as two phase systems, the colloidal phase consisting of ultramicroscopic particles and holding a large quantity of water. When a dissolved substance is distributed between the water phase and the colloid phase, it is necessary to distinguish between the part which is irreversibly absorbed by the colloid and the part which is reversibly distributed between the two phases. In some cases, as, for example, with invertase, emulsin, and maltase, the amount of dissolved substance irreversibly absorbed by the colloid appears to be negligibly small. As the concentration of the dissolved substance (for example, sucrose) in the water phase increases, the concentration in the colloidal phase increases also, but more slowly, and from a certain point onwards is practically constant. This influence of concentration on the adsorption is very similar to the influence of concentration on the rate of inversion of sucrose by invertase, so that the law of partition of a dissolved substance between a colloid and water and the rate at which the partition takes place have an important bearing on the velocity of any reaction induced by the colloid.

J. C. P.

Isodimorphism. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1905, **140**, 447—449).—Two substances, which are not isomorphous in their

stable, crystalline forms, are capable of forming mixed crystals in which the stable form of one compound preponderates, the other being present in an unstable, isomorphous form; thus, if *Ab* represent the biaxial modification of one component and *Cu* the uniaxial modification of the other, then a certain number of cases of isodimorphism are known in which mixed crystals of the type *Ab,Cb* or *Cu,Au* are formed; up to the present, however, the series has not been extended to include mixed crystals of the type *Ab,Cu* or *Au,Cb*. In the present paper, the author describes three types of mixed crystals formed by potassium and rubidium nitrates; the first two, namely, *Ab,Cb* and *Ab,Cu* are obtained by crystallising from water the salts mixed in varying proportions, whilst the third type, *Au,Cu*, is obtained by fusing a mixture of the salts in which rubidium nitrate preponderates. M. A. W.

Calculation of Atomic Weights. JULIUS MEYER (*Zeit. anorg. Chem.*, 1905, 43, 242—250).—The various errors introduced during the calculation of atomic weights are considered. A. McK.

Molecular Weight Determinations by means of Platinum Thermometers. HOWARD T. BARNES, EBENEZER H. ARCHIBALD, and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1905, 27, 47—49).—A description is given of apparatus involving the use of platinum thermometers which has been devised for ebullioscopic determinations, a differential method of temperature measurement being employed. The apparatus is said to be superior to that in which mercury thermometers are used, since there is no necessity either for adjustment for liquids having different boiling points or for any tapping device. No error can be introduced by changes in the atmospheric pressure and the thermometer can be made of any degree of sensitiveness. A diagram of the apparatus is given.

The results of some determinations of the molecular weights of potassium chloride, nitrate and sulphate in aqueous solutions are appended. E. G.

Efficiency of Centrifugal Purification. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1905, 27, 104—111).—Quantitative experiments are described which show that the purification of crystals can be effected with a considerable saving of time, labour, and material by means of centrifugal draining and washing. It is shown, for example, in the case of sodium nitrate containing free nitric acid as an impurity that with two crystallisations the salt obtained with the aid of centrifugal draining and washing is 2000 times as pure as that obtained by ordinary gravitational draining, and that for the attainment of an equal degree of purity the yield is about 100 times as great by the centrifugal process as by the ordinary method of draining.

Special forms of apparatus have been devised for the manipulation of small quantities of material. For an account of these, the description and diagrams in the original must be consulted. E. G.

Electric Furnaces for Laboratory Use. BERTRAM BLOUNT (*Analyst*, 1905, 30, 29—35).—The first combustion furnace described

is one in which a porcelain tube of $\frac{3}{4}$ inch diameter is placed inside a shorter and wider fireclay tube of about 1 inch internal diameter, so that about 3 inches of the inner tube project at each end. The space between the two tubes is filled with resistance material, consisting of retort carbon mixed with varying quantities of siloxicon or carborundum. Two short copper tubes fitting closely into the space between the tubes at both ends serve to conduct the current to the resistance material.

In the second furnace, two concentric fireclay tubes surround, but do not touch, that part of the porcelain tube to be heated. The resistance material is packed between these fireclay tubes and the current led in by means of an annular copper disc at each end. If the space between the tubes be very narrow, retort carbon may be used alone; otherwise, the resistance must be increased by adding varying amounts of siloxicon. The two tubes are surrounded by two other wider fireclay tubes, which in turn are wrapped with asbestos to retain the heat. The ends of the furnace are made of uralite discs, which also support the porcelain tube.

For ultimate organic analyses, the furnace can be made in sections, to allow for progressive heating.

W. P. S.

Apparatus for Preparing Hydrogen or Carbon Dioxide.
MAX ÜBEL (*Chem. Zeit.*, 1905, 29, 141).—An apparatus constructed on the Debray principle, for the details of which the original must be consulted.

L. DE K.

Inorganic Chemistry.

Action of Persulphates on Haloids. MAX DITTRICH and H. BOLLENBACH (*Ber.*, 1905, **38**, 747—751. Compare Abstr., 1904, ii, 80; Marshall, Abstr., 1901, ii, 156).—Silver chloride, bromide, and iodide, are not acted on by ammonium persulphate in warm dilute nitric acid solution, but, if a small quantity of silver nitrate is present, the silver haloid is partly oxidised to chlorate, bromate, or iodate respectively. The oxidation takes place most easily with the iodide, and, if the warming is continued, may be in that case complete.

G. Y.

Chemical and Geological History of the Atmosphere. JOHN STEVENSON (*Phil. Mag.*, 1905, [vi], **9**, 88—102).—A continuation of previous papers (*ibid.*, 1900, [v], **50**, 312, 399; 1902, [vi], **4**, 435), in which the conclusion was arrived at that in earlier geological history the atmosphere was far more extensive, contained no free oxygen, but contained very much more carbon dioxide as well as, probably, hydrogen and hydrocarbons. The quantity of carbon dioxide diminished in early geological epochs by vegetation and weathering of rocks, and

the author considers that, after a certain point in this abstracting process was reached, the quantity of carbon dioxide in the atmosphere probably became variable, that is, alternately increased or diminished according to the relative activity of the forces or reactions which produced it and the counteracting forces or reactions. The various productive and removing agencies are considered and the author shows how slight variations in volcanic activity and other telluric phenomena may affect the quantity of carbon dioxide. Lecher considered that carbon dioxide and not aqueous vapour is the chief cause of the absorption of solar radiation in our atmosphere (Abstr., 1881, 489), and from this the author elaborates the idea that the variations in the quantity of carbon dioxide in the atmosphere are sufficient to account for, and were probably the cause of, the great differences of climatic conditions during geological history.

L. M. J.

Formula of Hyposulphurous Acid. AUGUST BERNTHSEN (*Ber.*, 1905, 38, 1048—1056).—The formula of hyposulphurous acid is discussed in connection with the recent work of Baumann, Thesmar, and Frossard on formaldehyde sodium hyposulphite (this vol., i, 260), who claim that the constitution $\text{H}_2\text{S}_2\text{O}_4$ was not established by the controversy between Bernthsen and Schützenberger (Abstr., 1882, 461).

It is here claimed that sodium hyposulphite is a chemical individual, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and not a double salt, $\text{NaHSO}_3 \cdot \text{NaHSO}_3 \cdot \text{H}_2\text{O}$; that the terms hyposulphite and hyposulphurous acid are already in use for compounds of the type $\text{R}_2'\text{S}_2\text{O}_4$, and, therefore, not available for naming other compounds, and, lastly, that compounds of the type $\text{R}'\text{HSO}_2$ or $\text{R}_2'\text{SO}_2$, are best termed salts of sulphonylic acid, the formaldehydesulphonylates being already known.

E. F. A.

Hyposulphurous Acid. MAX BAZLEN (*Ber.*, 1905, 38, 1057—1068. Compare preceding abstract).—Hyposulphite solutions are technically prepared by the action of zinc on aqueous sodium hydrogen sulphite solutions and subsequent removal of the zinc with milk of lime or sodium hydroxide. Sodium hyposulphite is precipitated from this either by sodium chloride or hydrogen sulphite or by alcohol; it crystallises in glistening prisms of the formula $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The potassium salt, $\text{K}_4\text{S}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$, prepared in the same way from potassium hydrogen sulphite, sulphurous acid, and zinc, forms sulphur-yellow needles. The calcium salt, $\text{CaS}_2\text{O}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, is best prepared by the interaction of sodium hyposulphite and calcium chloride under the exclusion of air; it separates in minute, sparingly soluble needles. The zinc salt is easily soluble; zinc double salts, as for example, $\text{ZnNa}_2(\text{S}_2\text{O}_4)_2$, are readily formed but not very characteristic. To dehydrate the foregoing salts, the well-stirred suspension in dry alcohol is heated at from 65—70°; technically an alcoholic paste of the salt is extracted in a Soxhlet apparatus with boiling alcohol, which is continually dried by quicklime.

Very stable sodium, potassium, calcium, and zinc salts of the type $\text{R}_2'\text{S}_2\text{O}_4$ are thus obtained.

Sodium formaldehydesulphonylate, $\text{NaSCO}_3\text{H}_3 \cdot 2\text{H}_2\text{O}$, obtained by the

interaction of sodium hyposulphite, formaldehyde and sodium hydroxide, crystallises from water in prisms or from hot alcohol in silver, glistening leaflets. With barium hydroxide, it forms a precipitate of a *barium* salt, $\text{BaSCO}_4\text{H}_4\cdot\text{H}_2\text{O}$, crystallising in needles grouped in stellar aggregates. *Sodium benzaldehydesulphoxylate*, $\text{NaSO}_3\text{C}_6\text{H}_5$, forms large, glistening crystals sparingly soluble in water. E. F. A.

Time Interval before Precipitation is observed in Thio-sulphate Solutions. GASTON GAILLARD (*Compt. rend.*, 1905, 140, 652—655. Compare von Oettingen, *Abstr.*, 1900, ii, 400).—Curves are given showing the influence of the concentration of the sodium thiosulphate and of the added acid on the time which elapses before the separation of sulphur is observed. Various acids and thiosulphates have been examined. The presence of salts (chlorides, bromides, iodides, sulphites) in the thiosulphate solutions retards the appearance of the opalescence. On addition of equal volumes of water, glycerol, and alcohol to the same volume of 5 per cent. sodium thiosulphate solution, the observed retardations are different, the greatest effect being produced by the alcohol, the least by the water. H. M. D.

Action of Hydrogen Sulphide on Selenious Acid. II. Selenium Sulphide. ALEXANDER GUTBIER and JOHANN LOHMANN (*Zeit. anorg. Chem.*, 1905, 43, 384—409. Compare this vol., ii, 84).—The authors have investigated the question as to whether the products obtained by the action of hydrogen sulphide on selenious acid or by the action of hydrogen selenide on sulphurous acid are mixtures or compounds of selenium and sulphur.

The orange-red product prepared by the action of hydrogen sulphide on an aqueous solution of selenious acid in the absence of air and of light contained 58.1 per cent. of selenium and 41.8 per cent. of sulphur, whilst the product obtained under pressure contained 17.63 per cent. of selenium and 82.27 per cent. of sulphur, whereas SeS_2 requires $\text{Se} = 55.23$ and $\text{S} = 44.77$ per cent. At the ordinary temperature, in the presence of air, a product is obtained which, when heated, becomes red and has the formula SeS_2 ; at higher temperatures, a product richer in selenium is obtained and at lower temperatures the product contains more sulphur than selenium. These results indicate that a compound is not formed. At the ordinary temperature, hydrogen sulphide acts as a reducing agent according to the equation $\text{H}_2\text{SeO}_3 + 2\text{H}_2\text{S} = \text{Se} + \text{S}_2 + 3\text{H}_2\text{O}$. At higher temperatures, the liberated sulphur is oxidised to sulphur trioxide.

From the mixture obtained by the action of hydrogen sulphide on selenious acid, the sulphur can be mechanically separated by extraction with a mixture of benzene and carbon disulphide.

The results are comparable with those of Gutbier and Flury on the reduction of tellurous acid by hydrogen sulphide (*Abstr.*, 1903, ii, 71).

The authors have not been able to isolate the sulphide, SeS , described by Ditté.

The hydrosol obtained by passing hydrogen sulphide into an aqueous solution of selenium dioxide also does not contain selenium

and sulphur chemically combined, since, when the solution is repeatedly agitated with carbon disulphide, the total amount of sulphur present can be separated.

A. McK.

Electrochemical Equivalent of Tellurium. GINO GALLO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 23—28 and 104—109. Compare Abstr., 1904, ii, 639).—The voltameter employed by the author was tested by electrolysing copper sulphate solution in series with a silver voltameter, the values obtained for the atomic weight of copper varying from 63·50—63·66, the mean being 63·58. The electrolytic deposition of tellurium was carried out in series with two silver voltameters; as a mean of 12 determinations, the number 127·61 was obtained for the atomic weight of tellurium ($\text{Ag} = 107·93$).

T. H. P.

Electrolytic Oxidation of Ammonia to Nitrites. ERICH MÜLLER and FRITZ SPITZER (*Ber.*, 1905, 38, 778—782. Compare Traube and Biltz, Abstr., 1904, ii, 727).—In the presence of a small amount of sodium hydroxide, ammonia may be oxidised electrolytically to nitrite even in the absence of copper compounds.

In the presence of copper hydroxide and sufficient alkali, the oxidation of ammonia to nitrite does not cease suddenly when the nitrite concentration has reached a certain value, but appears to proceed quite independently of the nitrite concentration. In these experiments, the oxidation was allowed to proceed for a comparatively short time only, so that the amount of alkali present was not greatly reduced. The formation of nitrite is intimately connected with the amount of alkali present, and when no sodium hydroxide is present, but only ammonia, nitrite, and copper hydroxide, it is found that the nitrite is transformed into nitrate more rapidly than the ammonia into nitrite, and thus the concentration of the nitrite tends to decrease.

Nitrogen is also formed during the oxidation.

J. J. S.

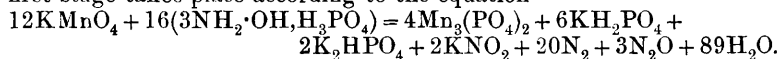
Electrolytic Oxidation of Ammonia. WILHELM TRAUBE and A. SCHÖNEWALD (*Ber.*, 1905, 38, 828—831. Compare Abstr., 1904, ii, 727).—In continuation of the previous experiments, the influence of changing the concentration of the free alkali or ammonia on the rate of the electrolytic oxidation of ammonia has been investigated. In presence of much ammonia, the amount of nitrite can be increased to about 11 per cent. before oxidation to nitrate begins, whilst from an 11 per cent. nitrite solution to which ammonia, sodium hydroxide, and copper hydroxide had been added a solution containing as much as 17 per cent. nitrite was obtained on hydrolysis. The paper includes a claim for priority (compare Müller and Spitzer, preceding abstract).

E. F. A.

Action of Potassium Permanganate on the Salts of Hydroxylamine (Nitrate, Phosphate, Arsenate). LOUIS J. SIMON (*Compt. rend.*, 1905, 140, 659—661).—When decinormal potassium permanganate is added to a neutral solution of hydroxylamine nitrate until the solution assumes a yellow tint, it is found that 0·4 molecules of the permanganate are required for each molecule of hydroxyl-

amine in accordance with the equation $2\text{KMnO}_4 + 5(\text{NH}_2\cdot\text{OH}, \text{HNO}_3) = 2\text{Mn}(\text{NO}_3)_2 + 2\text{KNO}_3 + 2\text{N}_2\text{O} + 10\text{H}_2\text{O}$. If the solution is acidified at this stage, the nitrite is oxidised and a further quantity of permanganate equal to 0.16 molecule for each molecule of hydroxylamine can be added to the solution before the latter assumes the pink colour of the permanganate. When hydroxylamine chloride or sulphate is employed instead of the nitrate, only one-half of the above quantity of permanganate is used up in the second stage.

When the phosphate or arsenate is employed, the oxidation in the first stage takes place according to the equation



Each molecule of hydroxylamine requires 0.25 molecule of permanganate. If the solution is acidified at this stage, a further 0.166 molecule of permanganate is reduced per molecule of hydroxylamine.

If the hydroxylamine solutions are acidified at the outset, the reducing power is increased. The molecular ratio permanganate | hydroxylamine is not quite constant, but oscillates around the value 0.8. If the acidity is too feeble or too strong, the maximum reducing power is not attained. The value of the reducing power depends also to some extent on the temperature and on the rapidity of titration. It is evident, therefore, that hydroxylamine cannot be accurately estimated by direct titration with permanganate in acid solution.

H. M. D.

Nitroxyl Chloride. ALEXANDER GUTBIER and JULIUS LOHMANN (*J. pr. Chem.*, 1905, [ii], 71, 182—195).—The authors confirm the statements of Williams (*Trans.*, 1886, 49, 222) that nitroxyl chloride is not formed by the action of chlorine on nitrogen peroxide, and of Geuther (*Abstr.*, 1888, 785) that the product of the action of nitrogen peroxide on phosphoric oxide is nitrosyl chloride. As no chlorinated product could be obtained by acting on silver nitrate with chlorine (Odet and Vignon, *Compt. rend.*, 1869, 69, 1142), nitroxyl chloride has not yet been prepared.

G. Y.

Attempts to Prepare Absolute Nitric Acid. FRIEDRICH W. KÜSTER and SIEGMAR MÜNCH (*Zeit. anorg. Chem.*, 1905, 43, 350—355).—Nitric acid containing 98.5 per cent. of HNO_3 was partially frozen, the liquid removed, and the almost pure nitric acid thus obtained fractionated by crystallisation in an apparatus described. By continued fractionation, products were soon obtained of constant freezing point, that is, the temperatures at which successive fractions began to crystallise were constant. As solidification, however, proceeded, the temperature fell appreciably, and this indicated that an impurity was present which could not be removed by fractional crystallisation. The acid obtained in this manner contained 99.4 ± 0.1 per cent. of HNO_3 .

Absolute nitric acid exists only in the form of snow-white crystals at a temperature below -41° . Nitric acid crystals melt to a yellow liquid, which is a solution of nitrogen pentoxide and water in nitric acid. Whilst solid nitrogen pentoxide is colourless, the liquid has not

yet been obtained colourless. This liquid, in presence of dry air, becomes colourless, the pentoxide being removed and the water remaining. The liquid obtained after removal of the pentoxide contained 98.67 per cent. of HNO_3 .

When dry air was passed into an acid containing 99.4 per cent. of HNO_3 , the yellow colour of the acid disappeared exactly at the point when the percentage of HNO_3 was 98.67. A. McK.

The Phosphorescence of Phosphorus. ÉMILE JUNGFLAISCH (*Compt. rend.*, 1905, 140, 444—447).—The phosphorescence of phosphorus is commonly attributed to the combustion of phosphorus vapour; the author, however, finds (1) that the tension of phosphorus vapour at the ordinary temperature is too low to account by its combustion for the relatively intense luminosity of the phosphorescence, (2) that phosphorus in contact with even small quantities of oxygen is converted into an oxide much more volatile than phosphorus, which by its spontaneous combustion gives rise to the luminous phenomenon of phosphorescence. The investigation on the nature of the lower oxide is not yet complete, and the present paper contains a description of experiments which establish the two points stated above. A current of dry carbon dioxide freed from traces of oxygen by contact with heated copper, and then saturated with phosphorus vapour at 15° by passing over pure dry phosphorus, becomes only very faintly luminous when it comes in contact with the air, and the amount of phosphorus present as vapour in one litre of the gas at 15° , and under normal pressure is 0.000535 gram; if, however, a very small quantity of air be mixed with the carbon dioxide before it passes over the phosphorus, the issuing gas becomes intensely luminous in contact with the air, than which also it is specifically heavier; the phosphorescent oxide is partly condensed when cooled at -10° , the condensing tube containing in addition a small quantity of phosphoric oxide and of the oxide P_4O (compare, however, Burgess and Chapman, *Trans.*, 1901, 79, 1235).

M. A. W.

Red Phosphorus. RUDOLF SCHENCK (*Zeit. Elektrochem.*, 1905, 11, 117—118).—The name "red phosphorus" includes a large number of products the properties of which differ considerably from each other and depend on the temperature at which the substance has been prepared. Hittorf's red phosphorus, crystallised from lead, stands at one end of the series and is the only well defined member of it. When yellow phosphorus is heated, its vapour pressure remains constant until all the yellow phosphorus has disappeared; the vapour pressure does not then fall at once to that of red phosphorus, but diminishes quite gradually. This points to the product first obtained being a solution of yellow in red phosphorus. This view is supported by the behaviour of solutions of phosphorus. A solution of yellow phosphorus in phosphorus iodide deposits red phosphorus at 100° , a solution in P_4S_3 at about 300° , and a solution in phosphorus tribromide at its boiling point. The red phosphorus so obtained is bright scarlet in colour, and it contains large quantities of the solvent. That deposited from phosphorus tribromide at 30° (by the action of light) contains

47.6 per cent. of the solvent, at 140° , 36.3 per cent., at 185° , 27.1 per cent., and at 218° 23.6 per cent. It is amorphous. The red phosphorus first deposited from yellow phosphorus by heat alone closely resembles that obtained from solvents. Scarlet phosphorus is very readily oxidised; it phosphoresces in ozone, although not in air. It is turned deep black by ammonia, piperidine, and other primary and secondary amines, a solution of potassium hydroxide in aqueous alcohol dissolves it, yielding a deep red solution. From this solution, acids precipitate a yellow, solid hydride of phosphorus mixed with bright red, finely divided phosphorus. The yellow, solid hydride behaves in much the same way as scarlet phosphorus itself towards piperidine and alcoholic potash. Determinations of the depression of the freezing point of yellow phosphorus by dissolving the hydride in it showed that the molecule of the latter is $P_{12}H_6$.

When scarlet phosphorus is heated for a long time, it becomes more and more like the red phosphorus of commerce, its colour becomes deeper and its reactivity less. Scarlet phosphorus is therefore only very finely divided amorphous red phosphorus, related to ordinary red phosphorus in much the same way that precipitated silica is related to quartz glass.

T. E.

Yellow and Red Arsenic Trisulphides. HEINRICH WINTER (*Zeit. anorg. Chem.*, 1905, 43, 228—235).—A contribution to the study of colloids. To a colloidal solution of arsenic trisulphide in water, prepared by passing an excess of hydrogen sulphide into an aqueous solution of arsenic trioxide and then removing the hydrogen sulphide, ammonium chloride, sulphate, nitrate, acetate and carbonate were added respectively. After the precipitate obtained in each case had subsided, the supernatant liquid was free from arsenic. Analysis of each deposit showed that the arsenic trisulphide had been quantitatively separated from the colloidal solution. The rate of coagulation was most rapid with ammonium chloride and slowest with ammonium carbonate.

The red modification of arsenic trisulphide was obtained by freezing the yellow colloidal solution, when the solid red form separated along with ice. It may also be conveniently obtained by evaporating the colloidal solution on the water-bath. When yellow arsenic trisulphide, obtained by the addition of electrolytes to the colloidal solution, was heated in an air oven at 100° , it was transformed into a red, vitreous mass; the yellow arsenic trisulphide obtained by passing hydrogen sulphide into a solution of arsenic trioxide in hydrochloric acid does not, however, undergo a similar change at 100° unless it is completely freed from hydrochloric acid. The red form is gradually transformed into the yellow on exposure to the atmosphere for 5—6 weeks at the ordinary temperature, or by being heated for some time at 150 — 160° .

Golden-yellow leaflets of arsenic trisulphide are formed in small amount when hydrogen sulphide is passed into an $N/5$ solution of arsenic trioxide in water. The formation of this modification increases in amount with increase of concentration of arsenious acid up to $3/10N$; as the concentration is still further increased, the

amount diminishes. Traces only are formed with *N*/20 solutions of arsenious acid.
A. McK.

The Perborates. PETR G. MELIKOFF (*Compt. rend.*, 1905, 140, 502).—A claim for priority (compare Jaubert, this vol., ii, 26, Melikoff and Pissarjewsky, *Abstr.*, 1898, ii, 332, 374; 1899, ii, 298).
M. A. W.

Perborates. J. BRUHAT and H. DUBOIS (*Compt. rend.*, 1905, 140, 506—509).—The perborates stable in the solid state are readily decomposed in aqueous or acid solution, liberating oxygen which, in the nascent state, combines with the water present to form hydrogen peroxide, hence the salts act as strong oxidising agents, liberating iodine from potassium iodide, oxidising chromic to perchromic or molybdic to permolybdic acid, ferrous to ferric salts, mercurous salts to yellow mercuric oxide, lead hydroxide to lead plumbate, and manganous salts to manganese dioxide; they also give an intense blood-red coloration with sulphuric acid solutions of titanous acid or sodium vanadate. *Uranyl perborate*, UO_4 , is a yellow, stable compound obtained by the action of a perborate solution on uranium dioxide. *Potassium di-perborate*, $\text{KB}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, is precipitated by alcohol from a solution of potassium diborate in hydrogen peroxide, contains 18·06 per cent. of active oxygen, and loses $1\text{H}_2\text{O}$ in a vacuum over phosphoric anhydride. *Ammonium perborate*, $\text{NH}_4\text{BO}_3 \cdot \text{H}_2\text{O}$, contains 16·84 per cent. of active oxygen. Sodium perborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, obtained by the electrolysis of a solution of sodium orthoborate or by adding hydrogen peroxide to the solution (compare, however, Melikoff, preceding abstract, and Jaubert, this vol., ii, 26) or by saturating a solution of boric acid with sodium peroxide, contains 10·38 per cent. of active oxygen, and on careful dehydration loses gradually $4\text{H}_2\text{O}$, the anhydrous salt, NaBO_3 , containing 19·51 per cent. of active oxygen.
M. A. W.

Evolution of Carbon in Fuels. ISIDORE BAY and JUST ALIX (*Compt. rend.*, 1905, 140, 377—378).—The authors find that the carbon content of fossil fuels increases with the age of the fuel, whilst the hydrogen and oxygen diminish, and the results obtained by analysing fuels in the various stages of formation between cellulose and graphite show that the percentage of carbon rises rapidly from 44·44 in cellulose to 74·46 in pit coal, 89·29 in anthracite, and 93·86 in graphite; the percentage of oxygen falls from 44·39 in cellulose to 28·03 in lignite and 9·03 in pit coal, and the percentage of hydrogen drops rapidly from 4·82 in pit coal to 3·28 in anthracite and 0·1 in graphite, whilst the amount of nitrogen which is absent in cellulose reaches a maximum in peat and then diminishes normally. The analytical numbers quoted in the paper are the mean results of three hundred analyses of each fuel obtained from different sources.
M. A. W.

Atomic Weight of Silicon. W. BECKER and JULIUS MEYER (*Zeit. anorg. Chem.*, 1905, 43, 251—266).—An historical account of the

methods used in the determination of the atomic weight of silicon is given.

The authors employed silicon tetrachloride for their determinations. This boiled at 56.9° under 760 mm. pressure; its vapour pressure at various temperatures was determined, the results obtained being considerably lower than those of Thorpe (*Trans.*, 1880, 37, 327). In the purification of silicon tetrachloride, special precautions were taken to exclude water; silicon tetrachloride, finally purified by means of liquid air, melts at -89° . Glass bulbs filled with the tetrachloride were broken in a platinum crucible containing ice-cold water, the silicon being estimated as the dioxide. As a mean of eight experiments, the value $\text{Si} = 28.21$ ($\text{O} = 16$) was found. A. McK.

The Carbon Silicide of the Cañon Diablo Meteorite. HENRI MOISSAN (*Compt. rend.*, 1905, 140, 405—406. Compare this vol., ii, 43).—From the residue obtained by extracting with hydrochloric acid 53 kilograms of the meteoric iron, a sufficient quantity of carbon silicide was separated to identify it with the synthetical compound CSi already described (compare *Abstr.*, 1894, ii, 43). The meteoric compound forms hexagonal crystals of a green colour, the sp. gr., determined in a mixture of bromoform and methylene iodide, is between 3 and 3.2 , and it behaves towards such reagents as fused potassium nitrate, chlorate, or hydroxide, fused lead chromate, or the acids exactly in the same way as the synthetical compound. M. A. W.

Solubility of Lithium Carbonate in Solutions of Salts of the Alkali Metals. GUSTAV GEFFCKEN (*Zeit. anorg. Chem.*, 1905, 43, 197—201).—The solubility of lithium carbonate in aqueous solutions of potassium nitrate, potassium chloride, sodium chloride, potassium sulphate, potassium chlorate, sodium sulphate, ammonium chloride, and ammonium sulphate respectively in varying dilutions was determined. The solubility of lithium carbonate in the sodium and potassium salts examined is greater than in water, whilst the solubility is still further increased by ammonium salts. A. McK.

Solubility of Gypsum as affected by Size of Particles and by Different Crystallographic Surfaces. GEORGE A. HULETT (*J. Amer. Chem. Soc.*, 1905, 27, 49—56).—An account of the influence of the size of particles of calcium sulphate on its solubility has been given previously (*Abstr.*, 1901, ii, 493). Experiments have now been made for the purpose of ascertaining whether the different planes of a gypsum crystal vary in solubility. The results show that if there is any difference it is too small to be detected by the method employed, and that the values obtained for the solubility of gypsum by Hulett and Allen (*Abstr.*, 1902, ii, 656) in experiments in which the cleavage plane largely predominated are also the values for any plane of gypsum.

If powdered gypsum is shaken with water for three minutes, a supersaturated solution is produced, which requires seventeen days to reach a state of final equilibrium; if, however, plates of gypsum are used, the solution requires half a day or more to become saturated,

whereas most substances, under similar conditions, would form a saturated solution in about an hour. These facts explain the divergences in the solubility values of gypsum as given by different observers.

E. G.

Bologna Phosphorus [Phosphorescent Sulphides]. LUDWIG VANINO and J. GANS (*J. pr. Chem.*, 1905, [ii], 71, 196—200. Compare Forster, *Ann. Phys. Chem.*, 1868, [ii], 133, 236; Klatt and Lenard, *Abstr.*, 1890, 201; Mourelou, *Abstr.*, 1899, ii, 484; 1900, ii, 141).—Barium sulphide, prepared by heating barium thiosulphate, is only slightly fluorescent, but if a mixture of 60 grams of barium thiosulphate, 6 c.c. of a 0.5 per cent. alcoholic uranium nitrate solution, and 12 c.c. of a similar bismuth nitrate solution is heated at 1300° for three-quarters of an hour, the product exhibits a strong yellowish-green phosphorescence, which is best seen in the largest fragments; a similar effect is produced by thorium nitrate. The presence of bismuth and uranium increases still more the phosphorescence of strontium sulphide obtained from the thiosulphate. Strontium sulphide containing lead and thorium exhibits a whitish-blue phosphorescence, but with lead only the effect is very slight. The golden phosphorescence of Klatt and Lenard's strontium sulphide is intensified by the addition of calcium fluoride.

The compositions of several of the best mixtures for the production of phosphorescent sulphides are given. In the absence of sunlight, the phosphorescence is most rapidly excited by Heraeus' mercury lamp, more slowly by a powerful Auer lamp.

G. Y.

Solubility of Barium Sulphate. FRIEDRICH W. KÜSTER and GEORG DAHMER (*Zeit. anorg. Chem.*, 1905, 43, 348—349).—When barium sulphate is boiled with a concentrated aqueous solution of chromic chloride for 5 days, or with a solution of chromic chloride acidified with hydrochloric acid for 10 days, it is found that in the former case the solution has dissolved from 40—120 times as much barium sulphate as does water, and in the latter case 450 times as much.

A. McK.

Silicates. VI. EDUARD JORDIS and E. H. KANTER (*Zeit. anorg. Chem.*, 1905, 43, 314—319. Compare *Abstr.*, 1903, ii, 475, 542, 595; this vol., ii, 88).—The study of the action of alkali earths on silica has been continued, pure powdered quartz being used. The analytical figures are quoted. In the barium and strontium series the preparations first made exhibit a high percentage of water in comparison with those made later. Uniform substances were not obtained.

A. McK.

Silicates of the Alkaline Earths. EDUARD JORDIS (*Zeit. anorg. Chem.*, 1905, 43, 410—415).—Historical. In the course of his researches, the author had overlooked the work of Le Chatelier (*Ann. des mines*, 1887, [8], 11, 345—464).

A. McK.

Fluorides of the Heavy Metals. EGON BÖHM (*Zeit. anorg. Chem.*, 1905, **43**, 326—340).—*Mercurous fluoride*, $\text{Hg}_2\text{F}_2 \cdot 4\text{H}_2\text{O} \cdot 4\text{HF}$, prepared by the action of concentrated hydrofluoric acid on mercurous oxide, forms monoclinic crystals [$a:b:c = 0.5673:1:1.060$; $\beta = 105^\circ 10'$]. When carefully heated, it yields water, hydrogen fluoride, and mercuric oxide. *Copper fluoride*, $\text{CuF}_2 \cdot 5\text{H}_2\text{O} \cdot 5\text{HF}$, prepared from hydrofluoric acid and cupric oxide, forms blue, monoclinic crystals [$a:b:c = 0.7513:1:0.557$; $\beta = 105^\circ 10'$].

Nickelous fluoride, $\text{NiF}_2 \cdot 6\text{H}_2\text{O} \cdot 5\text{HF}$, and *cobaltous fluoride*, $\text{CoF}_2 \cdot 6\text{H}_2\text{O} \cdot 5\text{HF}$,

are isomorphous. The compound $\text{NH}_2 \cdot \text{HgF}$, prepared by the action of an excess of ammonia on mercurous fluoride, is a yellow, amorphous powder. The compound $\text{CuF}_2 \cdot 4\text{NH}_3 \cdot 5\text{H}_2\text{O}$, prepared by the action of an excess of ammonia on cupric fluoride, forms rhombic crystals. The compound $5\text{NiF}_2 \cdot 6\text{NH}_3 \cdot 8\text{H}_2\text{O}$, prepared by the action of an excess of ammonia on nickel fluoride, forms bright green crystals. The following compounds are also described: $\text{CoF}_2 \cdot 2\text{NH}_4\text{F} \cdot 2\text{H}_2\text{O}$; $\text{Co}(\text{NH}_3)_6(\text{NO}_3)_2\text{F}$; $\text{Co}(\text{NH}_3)_4\text{OHFNO}_3$.

The compound $[\text{Co}(\text{NH}_3)_4\text{F}_2]\text{Cl}$, prepared by the action of hydrofluoric acid on tetramminecarbonatocobalt chloride, forms dark red, rhombic crystals. The compound $\text{Co}(\text{NH}_3)_6\text{Cl}_2\text{F}$, prepared by the action of hydrofluoric acid on luteocobalt chloride, forms yellow prisms, whilst the compound $\text{Co}(\text{NH}_3)_6\text{F}_3$, obtained as a by-product, forms yellow crystals.

A. MCK.

Formation of Complex Compounds with Mercury Thiocyanate. HERMANN GROSSMANN (*Zeit. anorg. Chem.*, 1905, **43**, 356—369. Compare Abstr., 1904, i, 983; ii, 406).—Mercurous thiocyanate, like the mercurous haloids, dissolves in potassium thiocyanate to form the complex $\text{K}_2\text{Hg}(\text{CNS})_4$, whilst mercury separates; the action is represented as follows: $\text{Hg}_2(\text{CNS})_2 + 2\text{KCNS} \rightleftharpoons \text{K}_2\text{Hg}(\text{CNS})_4 + \text{Hg}$. Mercuric thiocyanate dissolves in an aqueous solution of potassium thiocyanate more readily than does mercurous thiocyanate. Measurements of concentration cells according to Bodländer's method showed that the tetrathiocyanate, $\text{K}_2\text{Hg}(\text{CNS})_4$, exists in solution; in very dilute solutions, some trithiocyanate also exists.

The complex constant of the tetrathiocyanate is 2.5×10^{22} , which is greater at the ordinary temperature than that of the bromide; it decreases with rise of temperature and at 52° is identical with that of the bromide.

The solubility product of mercuric oxide may be calculated from Bersch's results.

The close relationships existing between the bromine and the thiocyanate ions are indicated by the author's results.

A. MCK.

Bibliography of the Rare Earths. RICHARD J. MEYER (*Zeit. anorg. Chem.*, 1905, **43**, 416—492).—This bibliography is arranged chronologically, references being given to 777 papers, extending over the years 1751—1905.

A. MCK.

Electrolytic Preparation of Ceric Ammonium Nitrate. GIUSEPPE PLANCHER and G. BARBIERI (*Atti R. Accad. Lincei*, 1904, [v], 14, i, 119—120).—The preparation of ceric ammonium nitrate either from ceric salts or by the action of oxidising agents on cerous ammonium nitrate is not easy to carry out and does not give good yields. Its electrolytic preparation, which has been unsuccessfully attempted by various authors, may, however, be readily effected as follows. As anode is used a large sheet of platinum which is wrapped round a thin porous pot. The anodic space is filled with a concentrated solution of cerous ammonium nitrate (50 grams of cerous nitrate and 25 grams of ammonium nitrate in 200 c.c. of solution), whilst the porous pot contains nitric acid into which dips the platinum wire cathode. Using a current of 0.1—0.2 ampere per sq. dm. of anode surface, the oxidation is almost quantitative, part of the ceric ammonium nitrate being deposited from the liquid and the remainder being separated by evaporation. T. H. P.

Purification of Gadolinium, Atomic Weight of Gadolinium. GEORGES URBAIN (*Compt. rend.*, 1905, 140, 583—585).—From 1 kilogram of crude gadolinium earth containing only traces of europium and the element Z δ (compare Abstr., 1904, ii, 340, and this vol., ii, 35), the gadolinium was isolated by repeated fractional crystallisation of the double nitrate of nickel and gadolinium, $2\text{Gd}(\text{NO}_3)_3 \cdot 3\text{Ni}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$. The atomic weight of gadolinium was determined by converting the sulphate $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ into the oxide Gd_2O_3 , and the mean value thus obtained from 10 determinations on the first six fractions is 157.23, the limiting values being 157.04 and 157.35; the corresponding values obtained from the last five fractions is 157.25 with the limiting values 157.04 and 157.45 (compare Benedicks, Abstr., 1900, ii, 209). M. A. W.

Ultra-violet Spectrum of Gadolinium. Sir WILLIAM CROOKES (*Proc. Roy. Soc.*, 1905, 74, 420—422).—The gadolinium used in the experiments was purified by fractional crystallisation of the double nitrates of bismuth and magnesium with the rare earth nitrates. The phosphorescent spectrum of different specimens of gadolinium, purified in this manner, contains bands which the author has previously ascribed to a new element, victorium (Abstr., 1899, ii, 751). The new observations confirm the supposition that victorium is present in the gadolinium as an impurity. H. M. D.

Monazite Earths. WILHELM FEIT and CARL PRZIBYLLA (*Zeit. anorg. Chem.*, 1905, 43, 202—214. Compare Muthmann and Weiss, Abstr., 1904, ii, 406).—The oxides of the cerium group of metals were separated from the crude product by the Demarçay-Drossbach method. The preliminary separation of cerium was not, however, effected, except when the crude material was particularly rich in it, and in such cases permanganate was used for its partial removal. The separation yielded five fractions: (1) a large quantity of lanthanum, much cerium, a trace of praseodymium; (2) much lanthanum, much cerium, little praseodymium, a trace of neody-

mium; (3) little lanthanum, much cerium, much praseodymium, little neodymium; (4) a trace of cerium, little praseodymium, much neodymium, little samarium, traces of other earths; (5) a small amount of neodymium, much samarium, much gadolinium, and other earths. From the first fraction, praseodymium was removed by continued crystallisation, whilst the cerium was removed by permanganate; the residual lanthanum was then completely separated as oxalate. From the third fraction, praseodymium was separated from lanthanum by aid of the sparing solubility of its nitrate, as contrasted with lanthanum nitrate.

Praseodymium oxalate forms a black superoxide.

Samarium was separated from the fourth fraction by repeatedly crystallising the latter.

The praseodymium was more difficult to remove; its separation was finally effected by crystallising the solution, to which a fresh amount of cerium magnesium nitrate had been added. The neodymium oxide obtained was blue with a violet lustre.

The fifth fraction was repeatedly crystallised until the neodymium was completely removed. The separation of samarium from neodymium by the magnesium double nitrate method in the presence of considerable amounts of more easily soluble earths is easily performed. By continued fractionation, the yellow earths were completely removed, since terbium does not form a magnesium double nitrate. Samarium magnesium nitrate crystallises with difficulty. The observation of Demarcay that the separation of the double nitrates takes place in the following sequence, neodymium, samarium (europium), gadolinium, is confirmed by the authors. From the mixture containing samarium (europium) and gadolinium, the former was separated as the double nitrate.

The separation of a mixture of oxides which was completely free from lanthanum, cerium, and praseodymium, but contained much neodymium, samarium, and gadolinium, and the total amount of terbium, holmium, erbium, ytterbium, and yttrium present in the original crude material is described. Lanthanum, cerium, praseodymium, neodymium, and samarium were separated in the pure form.

Atomic weight determinations of neodymium gave the value 144.5 and of samarium 151.2, where $O=16$ and lanthanum $=139.0$ (3 determinations in each case). The authors do not claim, however, that these figures are accurate, although the value for neodymium is almost identical with Auer von Welsbach's value, and the value for samarium agrees closely with that of Muthmann and Weiss. A. McK.

Terbium. WILHELM FEIT (*Zeit. anorg. Chem.*, 1905, 43, 267—281).

—A *résumé* of the literature on terbium is first given and the impurities mentioned to which the divergent values for the atomic weight of this element may be ascribed.

Thirty kilograms of monazite earths were freed from thorium (preceding abstract), the residue fractionated as magnesium double nitrate, the uncrystallisable fractions fractionated as nitrate in order to separate yttrium and erbium, and the more sparingly soluble nitrate again fractionated as the magnesium double nitrate. The mother

liquors from the latter crystallisation contained terbium together with samarium, holmium, erbium, yttrium, gadolinium, and ytterbium, the presence of the latter elements having been indicated spectroscopically. After 111 crystallisations, the greater portion of the terbium had accumulated in the more sparingly soluble fractions together with holmium, erbium, and yttrium. A further purification was effected owing to the varying solubility of the oxides of the different metals in their normal nitrates. Finally, crystallisation of the mixed oxalates was carried out. The preparation finally obtained gave the value for its atomic weight 158.6; it was a mixture of gadolinium oxide and terbium peroxide, and contained traces of holmium and yttrium. The amount of terbium present is more than 12 per cent.

A. McK.

Special Constituent obtained in the Tempering of an Aluminium Bronze. PIERRE BREUIL (*Compt. rend.*, 1905, 140, 587—590).—A copper aluminium alloy called *Fortior*, manufactured by Agésilas et Cie., contains traces of other elements, melts at 1010—1030°, has a singular point at 690—730°, and presents under the microscope a heterogeneous structure of white patches of copper or a compound of copper and aluminium embedded in a black matrix, probably the eutectic mixture. When tempered at 550°, much below the singular point, it becomes more homogeneous and granular; if the tempering be effected near the singular point, namely, between 650° and 750°, the structure of the metal changes, and a new constituent in the form of thin needles, similar to the martensite of tempered steels, appears embedded in the granular substance, and this change of structure is accompanied by a change in physical properties, namely, an increase in the elastic limit and breaking charge of the metal. As the temperature of tempering increases, the quantity of the martensitic constituent also increases, until at 950° it is the only constituent, and at the same time the elastic limit and the breaking charge are almost doubled. The effect of temper therefore on fortior is analogous to its effect on steels (compare Osmond, *Abstr.*, 1896, ii, 172); above the singular point, the fortior forms a solid solution, the crystalline form of which is not yet determined; the crystals break down at the singular point, giving rise to the constituents of the natural metal, and the effect of temper is to check this transformation.

M. A. W.

Blue Aluminium Compounds deposited on the Aluminium Anode. FRANZ FISCHER (*Zeit. anorg. Chem.*, 1905, 43, 341—347. Compare *Abstr.*, 1904, ii, 534).—When sulphuric acid of sp. gr. 1.175 is electrolysed with aluminium electrodes, layers of a bluish-green tint are deposited on the anode, especially when the electrolyte is kept cool; the portions of the deposit next to the electrode are, however, intensely blue. Microscopic examination indicated that this blue deposit is not a uniform substance. It is not acted on by distilled water. Dilute hydrochloric acid of such a strength as to act vigorously on aluminium at the ordinary temperature has scarcely any action on it. When warmed with hydrochloric acid, hydrogen is evolved, traces of silicic acid remaining: the filtrate gives a precipi-

tate with barium chloride and also contains aluminium. The product is free from sulphide and contains a basic aluminium sulphate, a little silicic acid, and traces of iron. When heated, it becomes white.

A. McK.

A New Process for making Electrolytic Iron. SERGIUS MAXIMOWITSCH (*Zeit. Elektrochem.*, 1905, 11, 52—53).—None of the processes described up to the present gives technically satisfactory results, the resulting iron being so brittle that it cannot be bent at all. A bath is made up to contain 20 per cent. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 5 per cent. of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; to 6 litres of this solution, 25 grams of sodium hydrogen carbonate are added; the skin of ferric hydroxide which forms on the surface protects the bath from oxidation; the precipitate is allowed to settle to the bottom and to remain undisturbed; a wrought iron anode and a copper cathode (thinly silvered and iodised) are used. The bath is kept continuously at work and 20 to 25 grams of sodium hydrogen carbonate added about twice a week. The iron formed improves in quality as time goes on, finally reaching a strength of 5180 kilos. per sq. cm., and being so soft that it can be bent at a sharp angle without breaking. The best current density is 0.3 ampere [per sq. decimetre?], and the current efficiency is 97—99 per cent. The author attributes the good results to the small concentration of the hydrogen ions in the bath, which prevents the deposited iron from containing occluded hydrogen. T. E.

Action of Dilute Acids on Ferrous Sulphide. ALFRED LIPSCHITZ and RUDOLF VON HASSLINGER (*Monatsh.*, 1905, 26, 217—225).—Pure ferrous sulphide reacts only extremely slowly with cold, dilute acids. "Active" ferrous sulphide, which evolves hydrogen sulphide with cold dilute acids, contains metallic iron; the hydrogen formed by the action of the acid on the free iron reduces the ferrous sulphide to hydrogen sulphide and iron, so that a small amount of free iron acts as an accelerator of the reaction.

When measured against a normal calomel electrode in a solution of ferrous sulphate and hydrogen sulphide in sulphuric acid, active ferrous sulphide has an *E.M.F.* -0.03 , which is identical with that of iron; in a solution of ferrous sulphate in sulphuric acid, inactive ferrous sulphide has an *E.M.F.* $+0.90$, which is similar to the *E.M.F.* of pyrites, $+0.89$, of marcasite, $+0.89$, and of magnetic pyrites, $+0.71$, whilst in the same solution iron has an *E.M.F.* -0.03 . G. Y.

Roussin's Salts [Nitrosulphides of Iron]. ITALO BELLUCCI and D. VENDITORI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 28—36).—An historical paper. T. H. P.

Nitrosulphides of Iron. ITALO BELLUCCI and D. VENDITORI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 98—104).—The authors show that all the methods employed by various investigators for the preparation of salts similar to that first described by Roussin (*Ann. Chim. Phys.*, 1858, [iii], 52, 285), to which he ascribed the formula $\text{Fe}_3(\text{NO})_4\text{S}_5\text{H}_2$, yield compounds of the constitution $\text{Fe}_4(\text{NO})_7\text{S}_3\text{X}'$. These salts con-

tain at least one molecule of water, which the authors consider may possibly be water of constitution and not of crystallisation. T. H. P.

Physical Properties of Pure Cobalt and Pure Nickel. H. COPAUX (*Compt. rend.*, 1905, 140, 657—659).—The cobalt was purified and freed from nickel by converting the chloride into pentammincobaltic chloride, recrystallising, and converting this into cobalt oxalate, which was reduced to metal by heating in an atmosphere of hydrogen. It was then melted in a crucible in a current of hydrogen, the current being interrupted as soon as fusion was complete. By this method of operating, oxidation of the metal and absorption of hydrogen were reduced to a minimum.

The nickel was freed from cobalt by precipitating the latter from hydrochloric acid solution with excess of potassium nitrite, the solution being saturated with a current of nitrogen trioxide. The nickel was separated from the mother liquor in the form of the ammonia compound, $\text{NiCl}_2 \cdot 6\text{NH}_3$, which was converted into the oxalate, and the latter reduced in a current of hydrogen. In fusing the metal, similar precautions were taken to those described in the case of cobalt. It was found difficult to prevent change during the operation, for the metal oxidises very readily and absorbs considerable quantities of hydrogen. On this account, the nickel samples used in the determination of the electrical resistance and the breaking weight were prepared by subjecting the reduced nickel to hydraulic pressure, forging, turning, and annealing in a current of hydrogen.

The two metals prepared as described differ appreciably in appearance; the cobalt is brilliant and silver-white in colour, the nickel is comparatively dull.

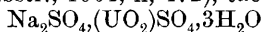
The following numbers are the measures of the physical properties examined :

	Cobalt.	Nickel.
Sp. gr. at 15° (water 4°=1)	8·8	8·8
Hardness	5·5	3·5
Melting point	1530°	1470°
Specific heat (20—100°).....	0·104	0·108
Electric resistivity (micro-ohms cm.) ...	5·5	6·4
Temperature-coefficient of resistivity ...	0·0055	0·0061
Breaking weight (kilograms per sq. mm.)	50	42

H. M. D.

Cobalt Chloride Tetrahydrate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1904, 1170—1171).—When anhydrous cobalt chloride is exposed to moist air, a tetrahydrate is formed; on further exposure, this is converted into the normal hexahydrate. T. A. H.

Synthesis of Sodium Uranyl Sulphate by Spring's Process. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1904, 1171—1172).—When uranic hydrate, $\text{UO}_3 \cdot \text{H}_2\text{O}$ (1 mol.), is mixed with sodium hydrogen sulphate (2 mols.) and the mixture compressed by Spring's method (*Abstr.*, 1904, ii, 472), the salt



is formed.

T. A. H.

Cryoscopy of the Sulphates. ALBERT COLSON (*Compt. rend.*, 1905, 140, 372—374. Compare Abstr., 1904, ii, 377, 532; this vol., ii, 34, 94).—A cryoscopic examination of aqueous solutions of Recoura's violet chromium sulphate (compare Abstr., 1892, 411; 1894, ii, 382) shows that it is truly isomeric with the green sulphate described by the author (this vol., ii, 94), the molecular complexity of the dissolved molecules being represented by $\text{Cr}_2(\text{SO}_4)_3$, and, further, the change to a green pentasulphate which occurs on boiling the violet solution is not accompanied by any change in the number of molecules, the freezing point of the solution after boiling remaining the same as before.

M. A. W.

Crystalline Chromic Phosphate. HUGO SCHIFF (*Zeit. anorg. Chem.*, 1905, 43, 304—307).—When sodium phosphate is added to an excess of a moderately concentrated aqueous solution of chrome alum, a reddish-grey gelatinous precipitate is first formed, which after 48 hours is transformed into dark violet, glistening crystals of chromium phosphate, $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$, which lose part of their water of crystallisation below 100° . The action is represented by the equation $2\text{KCrS}_2\text{O}_8 + 2\text{Na}_2\text{HPO}_4 = 2\text{CrPO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$.

At 100° , three molecules of water of crystallisation are lost.

If an excess of sodium phosphate is added, the violet, non-crystalline compound previously described by Rammelsberg, and also containing $6\text{H}_2\text{O}$, is formed. The green compound, $\text{CrPO}_4 \cdot 2\text{H}_2\text{O}$, is prepared by the action of acetic anhydride on the crystalline phosphate. The latter has the sp. gr. 2.121. Crystallographic measurements are appended.

A. McK.

Tungsten Hexafluoride. OTTO RUFF and FRITZ EISNER (*Ber.*, 1905, 38, 742—747).—The action of anhydrous hydrogen fluoride on tungsten hexachloride, in a copper-lined bomb, at the ordinary temperature leads to the formation of *tungsten hexafluoride*, WF_6 ; the product is passed over titanium tetrachloride to absorb the excess of hydrogen fluoride and then into a paraffin-lined glass vessel, cooled to -70° , at which temperature the product is solid. It vaporises without melting at -20° under half an atmosphere, or at slightly over 0° , under 1 atmosphere pressure, to a gas which fumes in moist air, is easily soluble in aqueous alkalis, attacks most metals, especially when containing traces of hydrofluoric acid, and forms tungstic acid when acted on by water. It forms double salts with alkali fluorides and attacks glass, and, even after a short time, paraffined glass, with formation of silicon tetrafluoride and tungsten oxyfluoride.

Molybdenum pentachloride reacts with anhydrous hydrogen fluoride, forming a gaseous *fluoride* resembling tungsten hexafluoride.

G. Y.

Oxyfluoride of Uranium. FEDÉRICO GIOLITTI and G. AGAMENNONE (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 114—119).—The authors find that the action of hydrofluoric acid on the saline oxide of uranium, U_3O_8 , to the products of which various compositions have been ascribed by different authors (compare Smithells, Trans., 1883, 43,

125), proceeds according to the equation $\text{U}_3\text{O}_8 + 6\text{HF} = \text{UOF}_2 + 2\text{UO}_2\text{F}_2 + 3\text{H}_2\text{O}$. The uranous oxyfluoride, UOF_2 , separates as a fine, green powder, whilst the oxyfluoride of sexavalent uranium, UO_2F_2 , is obtained as a yellow mass on evaporating the solution. A heavy green powder is also deposited, and this contains a larger proportion of fluorine than uranous oxyfluoride, and is possibly uranium tetrafluoride.

T. H. P.

Action of Silicon on Hydrated Metatitanic Acid. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, **43**, 370—372).—When hydrated metatitanic acid is heated with powdered, crystallised silicon, the mixture begins to glow vigorously before the temperature of the mixture has risen to a red heat. Water and hydrogen are formed. Anhydrous titanic acid does not behave in this manner when heated with silicon. The action probably proceeds according to the equation $2\text{TiO}(\text{OH})_2 + \text{Si} = \text{SiO}_2 + \text{Ti}_2\text{O}_3 + \text{H}_2\text{O} + \text{H}_2$. Amorphous silicon does not behave like the crystalline variety in this action. Silicon has no action on hydrated silicic acid, zirconic acid, or aluminium hydroxide.

Hydrogen is evolved when titanium is heated with hydrated metatitanic acid. When a mixture of zirconium and hydrated titanic acid is heated in the absence of air, little gas is evolved, whilst the titanic acid is strongly reduced.

The behaviour of tungsten towards hydrated metatitanic acid is similar to that of silicon.

Metatitanic acid in the dry state acts as a carrier of oxygen in these experiments, the oxygen of the hydroxyl group being conveyed to silicon, tungsten, and titanium respectively and the hydrogen liberated. The latter burns in the air, whilst the mixture glows and the titanium oxide is oxidised.

A. McK.

Zirconium Salts. ARTHUR ROSENHEIM and PAUL FRANK (*Ber.*, 1905, **38**, 812—816).—Zirconium hydroxide was heated with a saturated solution of hydrogen chloride in alcohol, the solution filtered from the excess of zirconium hydroxide, and hydrogen chloride passed into the filtrate. On addition of pyridinium chloride to the latter solution, the crystalline compound, $(\text{C}_5\text{NH}_5)_2, \text{H}_2\text{ZrCl}_6$, separated. With quinoline, the analogous compound, $(\text{C}_9\text{NH}_7)_2, \text{H}_2\text{ZrCl}_6$, was formed. The compound $(\text{C}_5\text{NH}_5)_2, \text{H}_2\text{ZrBr}_6$ is very unstable.

The compound $\text{Zr}_2\text{O}_3(\text{KSO}_4)_2, 8\text{H}_2\text{O}$, prepared by the addition of normal potassium sulphate to a cold aqueous solution of zirconium sulphate, crystallises in small plates. The following compounds were prepared: $\text{Zr}_2\text{O}_3(\text{RbSO}_4)_2, 15\text{H}_2\text{O}$ and $\text{Zr}_2\text{O}_3(\text{CsSO}_4)_2, 11\text{H}_2\text{O}$.

When an excess of freshly precipitated zirconium hydroxide is added to a hot concentrated solution of hydrogen potassium sulphate, the compound $\text{Zr}(\text{KSO}_4)_4, 3\text{H}_2\text{O}$ is precipitated as needles.

A. McK.

Metazirconic Acid. RUDOLF RUER (*Zeit. anorg. Chem.*, 1905, **43**, 282—303).—The changes undergone by an aqueous solution of zirconium oxychloride at the ordinary temperature and when boiled have been examined by the author. A new zirconium hydroxide is described, the relationship of which to the zirconium hydroxide already

known is the same as that of metastannic acid to ordinary stannic acid.

Zirconium oxychloride is suitable for the purification of zirconium earths. At the ordinary temperature, it undergoes hydrolysis in aqueous solution; this was proved by determinations of its electrical conductivity, which at first increases rapidly and attains to a constant value after 3 days. The behaviour of the aqueous solutions towards oxalic acid and ammonium oxalate in the presence of acids and sulphates also indicated that a hydrolytic change had occurred. When an aqueous solution of zirconium oxychloride is boiled for a short time, the hydrolysis undergone and the alteration of the analytical behaviour of the solution are marked. Such solutions form, for instance, with sodium sulphate and ammonium sulphate respectively, precipitates which are redissolved by an excess of precipitant; the precipitate, formed on the addition of dilute sulphuric acid, is slowly dissolved by an excess of the latter.

When a solution of zirconium oxychloride is boiled, the hydroxide formed by hydrolysis is transformed into another hydroxide, metazirconic acid. This transformation proceeds slowly, is perceptible after 2 hours, and is detected by a comparison of the colloidal hydroxide obtained from the cold and boiled solutions of the oxychloride respectively.

Metazirconic acid is best prepared by repeatedly boiling and subsequently diluting a 1 per cent. solution of zirconium oxychloride. Its reactions are analogous to those of metastannic acid. By concentrated hydrochloric acid, it is transformed very slowly into ordinary zirconium chloride. By the action of sulphuric acid on it, zirconium sulphate is produced.

Metazirconic acid, dried at 100° , has the formula $3\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$, whereas ordinary zirconium hydroxide, dried at 100° , has the formula $\text{ZrO}_2 \cdot \text{H}_2\text{O}$.

Colloidal solutions are formed by metazirconic acid and by its compounds with acids.

The two forms of zirconium hydroxide probably correspond with two different oxides. The oxide corresponding with ordinary zirconium hydroxide could not be obtained anhydrous; the oxide corresponding with metazirconic acid is probably the ordinary zirconium oxide.

The isomerism of the hydroxides of zirconium and of tin is also observed with the hydroxides of titanium and thorium. A. McK.

Uniform Nature of Thorium. RICHARD J. MEYER and A. GUMPERZ (*Ber.*, 1905, **38**, 817—825).—Baskerville (*Abstr.*, 1902, ii, 85; 1904, ii, 663) claims that thorium is a mixture of at least three elements. The experiments quoted by the authors are at variance with this view.

Baskerville does not quote sufficient detail as to the source of the thorium oxide used in his work. He determines the equivalent of thorium by converting a weighed quantity of the oxide into the anhydrous sulphate; his description is again inadequate and the method is faulty.

The authors dehydrated thorium sulphate octohydrate at 400° and determined the ratio $\text{Th}(\text{SO}_4)_2 : \text{ThO}_2$ by converting a weighed quantity of the anhydrous salt into the dioxide. The method was applied to the determination of the atomic weight of thorium in several of the chromate fractions obtained from thorium nitrate by Muthmann and Baur's method; the results do not indicate that thorium was not uniform.

When thorium chloride was sublimed in a current of chlorine in three fractions, the determinations of the atomic weight of the metal in these reactions yielded practically identical figures, corresponding with the recognised atomic weight of thorium. This result is at variance with Baskerville's.

A. McK.

Spectrographical Investigation of Some Thorium Preparations. G. EBERHARD (*Ber.*, 1905, 38, 826—828. Compare preceding abstract).—Examination of the spectrum of thorium preparations from various sources did not indicate that in any of these preparations thorium had been resolved into any new elements. Any observed variations from the spectrum of pure thorium could be accounted for by the ordinary impurities.

A. McK.

Halogen Double Salts of Quadrivalent Antimony. RUDOLF F. WEINLAND and HANS SCHMID (*Ber.*, 1905, 38, 1080—1087).—In the solution in hydrochloric acid an equilibrium exists between antimony tetrachloride and antimony tri- and penta-chlorides, according to the scheme $\text{SbCl}_3 + \text{SbCl}_5 \rightleftharpoons 2\text{SbCl}_4$. The amount of tetrachloride increases as the temperature is raised or the concentration of the hydrochloric acid increased. A salt, Rb_3SbCl_6 , is formed on adding rubidium chloride to such an equilibrium mixture, along with hot concentrated hydrochloric acid; it forms a black, microcrystalline powder composed of glittering octahedra and is at once decomposed by water. A salt, $\text{Rb}_2\text{SbCl}_6 \cdot 2\text{Rb}_3\text{SbCl}_6$, crystallising in brown, glistening, transparent, hexagonal plates, is formed if the equilibrium mixture is merely mixed with rubidium chloride at the ordinary temperature. With ammonium chloride, a series of salts has been obtained. From solutions containing quadrivalent antimony, ammonium chloride, and platonic chloride in hydrochloric acid, transparent brownish-violet to opaque black crystals, $(\text{NH}_4)_2(\text{Sb,Pt})\text{Cl}_6$, are obtained, according to the amount of platinum salt present. With tin tetrachloride, light to dark violet salts, $(\text{NH}_4)_2(\text{Sb,Sn})\text{Cl}_6$, are formed. A salt, $(\text{NH}_4)_2\text{SbCl}_6 \cdot (\text{NH}_4)_3\text{SbCl}_6$, is obtained in brown, glistening, hexagonal plates. The potassium salt, $\text{K}_5(\text{Sb,Pt})\text{Cl}_6$, forms a dark violet powder. The pyridine salt, $4(\text{SbCl}_6\text{H}_2 \cdot 2\text{C}_5\text{H}_5\text{N}) \cdot (\text{SbCl}_6\text{H}_3 \cdot 3\text{C}_5\text{H}_5\text{N})$, is obtained as a blackish-brown, crystalline powder, whilst $2(\text{SbCl}_6\text{H}_2 \cdot 2\text{C}_5\text{H}_5\text{N}) \cdot (\text{SbCl}_6\text{H} \cdot \text{C}_5\text{H}_5\text{N})$ crystallises in characteristic glistening, rhombic plates.

E. F. A.

Tantalum, its Preparation and Properties. WERNER VON BOLTON (*Zeit. Elektrochem.*, 1905, 11, 45—51).—Vanadium pentoxide, in the form of compressed powder, conducts electricity well at the ordinary temperature. Small rods of vanadium trioxide were made by heating rods of a plastic mixture of the pentoxide and paraffin in

powdered charcoal at 1700° for some hours. These rods were then attached to platinum wires and heated electrically in a glass vessel, which was continually exhausted by a mercury pump, when pure oxygen was evolved and a rod of metallic vanadium left. The melting point of the metal, determined photometrically, was 1680° .

Rods of columbium tetroxide were made and treated in the same way. The metal obtained was more ductile than vanadium and melted at 1950° .

Tantalum is prepared from the tetroxide in the same way, the white-hot oxide is decomposed electrolytically into oxygen and metal, which recombine sufficiently slowly to allow the oxygen to be removed. Larger quantities of the metal are prepared by a modification of Berzelius' method, which yielded a product containing 98.5 to 99 per cent. of the metal. This powder is compressed and heated in an electric arc in a vacuum, the oxides of tantalum fuse, and are dissipated in the form of dust much more readily than the metal, and it is possible to free the latter from them completely and thus obtain ingots of the perfectly pure metal. For commercial reasons, details of the methods employed are not given. The following physical constants of pure tantalum have been determined: specific heat, 0.0365; atomic heat, 6.64; sp. gr., fused metal, 16.64; wire, 0.05 mm. diameter, 16.5. When the wire is heated to whiteness in a vacuum, it becomes denser and crystalline, its sp. gr. finally reaching that of the fused metal. Coefficient of linear expansion from 0° to $50^{\circ} = 0.000079$. Specific resistance 0.165 ohm for a wire 1 metre long and 1 sq. mm. cross section. The resistance increases 0.3 per cent. per degree between 0° and 100° , and 0.26 per cent. per degree between 0° and 350° . In dilute nitric acid, tantalum stands between platinum and silver in its electrochemical properties. The modulus of elasticity of the wire (0.08 mm. dia.) was found to be 19,000 kilograms per sq. mm., its breaking stress, 93 kilograms per sq. mm.; this increases, however, as the diameter of the wire diminishes, reaching 150 to 160 kilograms per sq. mm. for wire 0.05 mm. thick. The extension of the wire before breaking is small, being only 1 to 2 per cent., notwithstanding which wires of 0.03 mm. diameter can be drawn. An ingot of the metal beaten out under the steam hammer to a sheet 1 mm. thick was drilled with a diamond drill making 5000 revolutions per minute for 72 hours continuously, after which a depression of about $\frac{1}{4}$ mm. was found, the diamond drill being much worn; the metal therefore combines extraordinary hardness with great ductility. Immersed in dilute sulphuric acid, tantalum only allows currents to pass when it is the cathode, when it is the anode no current passes even with 220 volts, owing to the formation of a film of oxide. Compact tantalum may be etched with hydrofluoric acid; the appearance of the surface is a good guide to the purity of the metal. The melting point of the pure metal is about 2250° ; its electrical dissipation as dust when used in a vacuum is extremely small. Many experiments with incandescent electric lamps made with a tantalum wire filament showed that their useful life is about the same as with a carbon filament, whilst the electrical energy consumed is less than half.

In making tantalum by the action of sodium on potassium tantalum fluoride, much hydrogen is evolved, part of which is absorbed by the

metal; it may be driven out by heating in a vacuum. Red-hot tantalum powder decomposes water, giving off hydrogen. When the powder is placed in a platinum dish containing dilute acid and is made the cathode, it takes up very large quantities of hydrogen, which is not driven off completely even by fusion, the fused metal being hard and brittle. Traces of hydrogen, however, do not affect its ductility. Compact tantalum, when heated in the air, becomes yellow at 400° , blue at a dull red heat, and is finally covered with a layer of the white pentoxide which protects the metal below it. Thin wire however, burns with a white light without flame. Metallic tantalum heated to whiteness does not combine with oxygen if its pressure is less than 20 mm.; this explains the possibility of preparing the metal by heating the oxide in a vacuum.

When heated in nitrogen, it becomes dull grey and brittle, the powdered metal combines readily with sulphur, selenium and tellurium. Iron alloys containing from 5 to 10 per cent. of tantalum are very hard and ductile. Silver does not alloy with tantalum at all, and the same is true of mercury. Molybdenum and tungsten alloy readily with it; the alloys containing less than 5 per cent. of these metals are ductile. More than 1 per cent. of carbon renders tantalum too brittle to be drawn into wire, but metal containing 0.5 per cent. of carbon can still be drawn into wire 0.1 mm. thick. Traces of carbon, boron, or silicon add to its hardness without diminishing its ductility. Boiling sulphuric, nitric, or hydrochloric acid or mixtures of these are without action on compact tantalum. Hydrofluoric acid acts on it very slowly unless the metal is in contact with platinum. Aqueous solutions of alkalis are also without action, but fused alkalis cause it to disintegrate.

T. E.

Supposed Allotropy of Gold. WILLEM J. VAN HETEREN (*Chem. Centr.*, 1905, i, 503; from *Chem. Weekblad*, 2, 47—53).—It has been stated by Julius Thomsen that different allotropic modifications of gold are obtained by the reducing action of sulphurous acid on various solutions of gold compounds. The supposed allotropic forms obtained by the reduction of (a) neutral auric chloride, (b) auric bromide, (c) aurous chloride, bromide, or iodide have been designated respectively as gold, gold_a , and gold_b . The author finds, that, when galvanic cells are constructed with gold and gold_a or gold and gold_b as reversible electrodes, the observed potential differences at 25° (0.4—0.6 millivolt) are not greater than when two samples of the first allotropic form are employed as electrodes.

From the values given by Thomsen for the heat changes accompanying the transformation of gold_a and gold_b into gold, a large temperature-coefficient of the *E.M.F.* of such cells would be expected. Measurements at 0° , however, gave the same result as at 25° .

H. M. D.

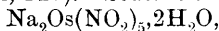
Electrolytic Solution of Platinum in Sulphuric Acid. ANDRÉ BROCHET and JOSEPH PETIT (*Compt. rend.*, 1905, 140, 655—657).—When a direct current of rapidly varying intensity is passed through a solution of sulphuric acid containing an anode of platinum, the latter

dissolves and platinum separates at the cathode. The addition of an oxidising agent diminishes the rate of solution of the platinum and also prevents its separation at the cathode. The electrolytic solution of the anode is not therefore due to a specific action of the alternating current, but is attributable to the rapidly alternating current density at the anode. The authors consider that Ruer's conclusions (Abstr., 1903, ii, 407) are untenable.

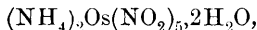
The phenomenon is quite different from that observed when an alternating current is passed through a cyanide solution between platinum electrodes. In this case, the electrolytic solution is due to pulverisation of the cathode in consequence of the primary formation of an alloy, which is attacked by water, the platinum being left in an altered physical condition in which it dissolves spontaneously in the cyanide solution (compare Abstr., 1904, ii, 414 ; 1905, ii, 27, 28).

H. M. D.

Some Osminitrites and an Osmium Nitrite. L. WINTREBERT (*Compt. rend.*, 1905, 140, 585—587).—Potassium osminitrite crystallises in canary-yellow, flattened parallelopipeds, very soluble in water (compare Abstr., 1903, ii, 221). *Sodium osminitrite*,

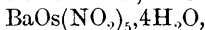


more soluble than the potassium salt, crystallises in flattened parallelopipeds of an orange-yellow colour. *Ammonium osminitrite*,

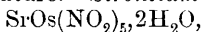


prepared by the action of ammonium sulphate on the barium salt, forms beautiful, orange-yellow crystals, stable in dry air and decomposed at 160° in an atmosphere of hydrogen, forming osmium peroxide.

Silver osminitrite, $\text{Ag}_2\text{Os}(\text{NO}_2)_5 \cdot 2\text{H}_2\text{O}$, forms golden-yellow crystals, stable in dry air. *Barium osminitrite*, $\text{BaOs}(\text{NO}_2)_5 \cdot \text{H}_2\text{O}$ and



are obtained by the action of barium chloride on a hot solution of potassium osminitrite, the monohydrate being obtained in the form of yellow plates above 15° , and the tetrahydrate in the form of amber-yellow needles at a lower temperature. *Strontium osminitrite*,



forms orange crystals; *calcium osminitrite*, $\text{CaOs}(\text{NO}_2)_5 \cdot 4\text{H}_2\text{O}$, orange-yellow plates; *magnesium osminitrite*, $\text{MgOs}(\text{NO}_2)_5 \cdot 4\text{H}_2\text{O}$, sulphur-yellow crystals, and *zinc osminitrite*, $\text{ZnOs}(\text{NO}_2)_5 \cdot \frac{1}{2}\text{H}_2\text{O}$, orange-yellow crystals. When a solution of barium osminitrite is precipitated by an equivalent quantity of sulphuric acid, a solution of osminitrous acid, $\text{H}_2\text{Os}(\text{NO}_2)_5$, is obtained, from which, on complete evaporation, *osmium nitrite*, $\text{Os}(\text{NO}_2)_3$, is obtained in the form of a deep brown powder.

M. A. W.

Mineralogical Chemistry

Iodobromite in Arizona. WILLIAM P. BLAKE (*Amer. J. Sci.*, 1905, [iv], 19, 230).—A soft, yellow mineral occurring as thin seams and crusts in a quartz and calcite vein near Globe, Pinal Co., Arizona, was found by its blowpipe reactions to contain silver, iodine, bromine, and chlorine; its identity with iodobromite is, however, not proved (compare iodembolite, *Abstr.*, 1902, ii, 403). L. J. S.

Formation of Oceanic Salt Deposits. XL. Limits of Existence of Tachyhydrite. JACOBUS H. VAN'T HOFF and L. LICHTENSTEIN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 232—235).—The experiments were made at 25° and consisted in determining the composition of solutions which were saturated with sodium chloride and also with one of the following systems: (1) calcium chloride, (2) magnesium chloride, (3) magnesium chloride and tachyhydrite, (4) potassium chloride, (5) potassium chloride and calcium chloride, (6) magnesium chloride and carnallite, (7) magnesium chloride, carnallite, and tachyhydrite, (8) carnallite and potassium chloride, (9) carnallite, potassium chloride, and calcium chloride, (10) tachyhydrite and calcium chloride, (11) tachyhydrite, calcium chloride, and carnallite. The results are represented in the usual graphical manner. J. C. P.

Action of Barium and Strontium Chlorides on Kaolin at High Temperatures. Z. WEYBERG (*Centr. Min.*, 1905, 138—142).—Kaolin, when fused for some time with an excess of barium chloride, gave a crystallised product having the composition $7\text{SiO}_2, 4\text{Al}_2\text{O}_3, 4\text{BaO}$; the crystals are hexagonal and hemimorphic, and are optically uniaxial and negative, thus agreeing with nephelite in physical characters. The corresponding strontium compound was obtained by a similar method. In both cases, the crystallised product contained also isotropic irregular grains with the composition $30\text{SiO}_2, 4\text{Al}_2\text{O}_3$. L. J. S.

Dumortierite. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1905, [iv], 19, 211—224).—A dyke in granite at Dehesa, San Diego Co., California, consists in the upper part of a fine-grained rock composed of quartz and sillimanite, whilst the lower part is a coarse rock consisting of quartz and dumortierite with small amounts of sillimanite and muscovite, &c. The dumortierite is lavender in colour, instead of the usual blue colour of this mineral, and forms irregular masses with ragged outlines or fan-shaped radiating masses several centimetres across. The pleochroism is marked, being colourless to deep reddish-purple. There is a prismatic cleavage parallel to (210). Measurement of imperfectly developed crystals from this and from two other American localities proves the mineral to be orthorhombic with the axial ratios $[a : b : c = 0.8897 : 1 : 0.6871]$. The chemical analysis of the mineral presents some difficulties; the mean of two analyses made on pure material gave the results under I. Regarding the titanium to

be present as Ti_2O_3 replacing alumina, the formula is deduced as $8\text{Al}_2\text{O}_3, \text{B}_2\text{O}_3, \text{H}_2\text{O}, 6\text{SiO}_2$, which may be written as $(\text{SiO}_4)_3\text{Al}(\text{AlO})_7(\text{BO})\text{H}$. This formula is similar to that of the closely allied mineral andalusite, $[(\text{SiO}_4)_3\text{Al}_3(\text{AlO})_3]$, and it explains the alteration of dumortierite to muscovite, $[(\text{SiO}_4)_3\text{Al}_3\text{KH}_2]$. The recent analyses by Ford (Abstr., 1903, ii, 158) are shown to agree with the new formula, except for a slight difference in the water, which was not determined directly in Ford's analyses.

	SiO_2 .	Al_2O_3 .	TiO_2 .	Fe_2O_3	H_2O .	B_2O_3 .	CaO .	Total.	Sp. gr.
I.	28.68	63.31	1.45	0.23	1.52	5.37	—	100.56	3.306
II.	28.51	59.75	0.95	2.48	2.12	5.54	0.68	100.03	—

A description is also given of the dumortierite from Skamania Co., Washington, which occurs as blue spherulites and brushes in a rock composed of andalusite, quartz, and muscovite; analysis of not quite pure material gave the results under II.

L. J. S.

The Billings Meteoric Iron. HENRY A. WARD (*Amer. J. Sci.*, 1905, [iv], 19, 240—242).—This iron was found near Billings, Christian Co., Missouri, in 1903. The weight before cutting was 54lbs., and it was much rusted on the surface. The structure is coarsely octahedral. Analysis by H. W. Nichols gave:

Fe.	Ni.	Co.	Cu.	Si.	P.	S.	Total.
91.99	7.38	0.42	0.01	0.08	0.15	0.06	100.09

L. J. S.

Physiological Chemistry.

Cheyne-Stokes Respiration. MARCUS SEYMOUR PEMBREY and RICHARD W. ALLEN (*Proc. Physiol. Soc.*, 1904—1905, xviii—xx; *J. Physiol.*, 32).—The gas analyses made lead to the conclusion that this form of breathing is due to a lessened excitability of the nervous system. The carbon dioxide accumulates, and the oxygen diminishes in the blood until at last the nerve-cells of the respiratory centre are stimulated, respiration begins and increases until the carbon dioxide is washed out and a large quantity of oxygen taken in; this is followed by lessening and then cessation of the respiratory efforts, the amount of carbon dioxide being insufficient to stimulate action until it again accumulates.
W. D. H.

Clinical Measurement of Electrical Conductivity. T. M. WILSON (*Amer. J. Physiol.*, 1905, 13, 139—153).—The electrical method of determining the relative volume of corpuscles and plasma gives results which agree well with hæmatocrite determinations. The

conductivity of serum is approximately the same as that of plasma. A small apparatus is described which can be used with only a small error for determining conductivity in a few drops of blood for clinical purposes. In thirteen healthy men, the conductivity of the blood varied from 35.3 to 52.6, and of serum from 84 to 111. In one healthy person over a period of five weeks the same numbers varied from 40.2 to 46.7 and 86.5 to 111 respectively. A few observations were also made in pathological cases.

W. D. H.

Action of Chloroform on the Blood-vessels of Bowel and Kidney. E. H. EMBLEY and CHARLES J. MARTIN (*J. Physiol.*, 1905, 32, 147—158).—The action of chloroform in the blood in such quantities as may occur with the inhalation of 1 to 3 per cent. of vapour in the air paralyses the neuro-muscular mechanism of the blood-vessels of the kidney and bowel, and this partly accounts for the fall of blood-pressure which occurs. Such results are not contradictory to those of Schäfer and Scharlieb (this vol., ii, 105), but supplementary; vessels in different parts may react in different ways to the same poison in different doses. The dilatation is mainly confined to the splanchnic area. The paper also contains a description of a new perfusion apparatus.

W. D. H.

Effect of Salts of Potassium and Ammonium and of Bile Salts on Blood Pressure. ARTHUR EDMUNDS (*Proc. Physiol. Soc.*, 1904—1905, xx; *J. Physiol.*, 32; *Brit. Med. J.*, 1905, i, 57—59).—A mere inspection of the crystals of choline platinichloride is insufficient to distinguish it from those of the potassium, ammonium and bile salts. A more detailed examination of its composition, solubilities, &c., is necessary. The present paper urges that combined with chemical testing, the investigation of the physiological action of the substance should be carried out. The fall of arterial blood pressure produced by choline is abolished if the animal has been previously poisoned with atropine. The other substances named above also produce a fall of arterial pressure if employed in solutions of sufficient strength, but in several points this differs from that produced by choline, notably in the circumstance that it is not abolished by atropine.

W. D. H.

Effect on Blood-pressure of Proteolytic Products. CHARLES G. L. WOLF (*J. Physiol.*, 1905, 32, 171—174).—Glycine, leucine, tyrosine, uracil, cytosine, indole, scatole, tryptophan, xanthine, hypoxanthine, guanine, thymine, glycine ethyl ester, pyrrolidine-2-carboxylic acid, α -methylpyrrolidinecarboxylic acid, arginine, or glutamic acid produces no fall of blood pressure when injected intravenously. These simple products of proteolysis do not produce the "peptone" effect; the latter is the result of a combination of groups. Nolf (*Abstr.*, 1904, ii, 425) states that a product of pancreatic autolysis which no longer gives the biuret reaction lowers the blood pressure. It is probable, however, that this is due to choline, a substance found in autolysed pancreas and yeast as a result of lecithin decomposition (Kutscher and Lohmann, *Abstr.*, 1903, ii, 670, 737). Levene's glucothionic acid produces a rise of blood pressure.

W. D. H.

Effect on Blood Pressure of Polypeptides. WILLIAM D. HALLIBURTON (*J. Physiol.*, 1905, 32, 174).—W. H. Thompson showed that the blood pressure lowering effect of "peptone" is mainly due to primary proteoses; the further proteolysis is continued, the less is the effect manifested. Similar results were obtained with protamines and protones. Crystalline cleavage products have not the power (see Wolf, preceding extract). Negative results were also obtained with four of Fischer's polypeptides (leucyl-leucine, leucyl-glycine, glycyl-asparagine, and alanyl-leucyl-glycine). The combinations of molecular groups necessary to produce the effect must therefore be more complex than the polypeptides. W. D. H.

Blood Ferments. ADOLF JOLLES and OPPENHEIM (*Chem. Centr.*, 1905, i, 546; from *Munch. med. Woch.*, 51, 2083—2085).—The catalases of the blood eliminate oxygen from oxyhæmoglobin; this is transferred to the tissues by oxydases. The catalase is destroyed by boiling and by acids. Various reagents differ in their effect on the ferments. The catalase is contained exclusively in the formed elements, its amount being roughly proportional to that of the hæmoglobin. No difference in this respect obtains in venous and arterial blood, or in that of men and women. The amount falls in tuberculosis, nephritis, and cancer. In a series of animals, the amount of catalase and the intensity of oxidation processes appear to go together. W. D. H.

Physico-chemical Researches on Hæmolysis. VICTOR HENRI (*Compt. rend.*, 1905, 140, 101—104).—The experiments presented relate to the hæmolysis produced in fowls by the serum of dog's blood, and have led to the following conclusions. The rapidity of hæmolysis is independent of the quantity of red corpuscles placed in contact with given amounts of serum, but a given amount of serum is only capable of hæmolysing a limited number of corpuscles. The velocity of action increases with increasing amounts of serum, but more rapidly than the increase of serum. It is only slow in the first 5 or 10 minutes, then increases rapidly, and diminishes again towards the end. If the total quantity of corpuscles hæmolysed at the end is represented by a , and the quantity hæmolysed at the end of t minutes is x , the fraction $\frac{1}{t} \log \frac{a}{a-x}$ is a constant. W. D. H.

Hydrolysis of Hepatic Glycogen produced by Injection of Amylase into the Portal Vein. PARISSET (*Compt. rend.*, 1905, 140, 534—537).—The quantity of sugar in the blood of the hepatic vein is increased by injecting a solution of amylase into the portal vein. This is considered to support the view that the normal change of glycogen is produced by an amylolytic ferment in the portal blood. W. D. H.

Assimilation of Calcium and Phosphoric Acid from Various Calcium Phosphates by Growing Animals. ALBIN KÖHLER, FR. HONCAMP, M. JUST, JUSTUS VOLHARD, M. POPP, and OTTO ZAHN (*Landw. Versuchs-Stat.*, 1905, 61, 451—479).—With the exception of

pure precipitated tricalcium phosphate, which is much more readily assimilated than degelatinised bone-meal, calcium phosphates which are only slightly soluble in Petermann's citrate solution are of slight feeding value. The highest results were obtained (in an experiment with only one lamb) when calcium diphosphate was given together with calcium lactate.

N. H. J. M.

The Gastric Mucous Membrane and Gastric Juice of the Pig. F. BENGEL and GUNNAR HAASE (*Pflüger's Archiv*, 1905, 106, 267—285, 286—312).—The cardiac region of the pig's stomach contains only an amylolytic ferment; the fundus region contains a peptic, an amylolytic, a rennetic, and a weak lipolytic ferment. In the pyloric region, the three first named are also present, but in smaller amount and not so active. The pepsin is most abundant in the fundus glands during the first hour of digestion; at the seventh hour, it falls, and rises again at the ninth or tenth. In the pyloric glands, it is at its maximum one or two hours later, and then falls until the end of digestion (12th hour). The fundus glands secrete more acid and more mucin than those in other regions. The other ferments vary in amount and activity at various times, so also does the acid.

W. D. H.

Chemico-physiology of Betaine. II. ALOIS VELICH and VLADIMÍR STANĚK (*Zeit. Zuckerind. Böhm.*, 1905, 29, 205—219).—The breaking-down of betaine in the digestive organs of a sheep increases as the time during which it is administered is increased, and as the nitrogen-content of the other food is diminished. The products of its decomposition are substances which yield ammonia and dimethylamine on hydrolysis, and are presumably urea and a methylated urea. The secretion of amino-acids in the urine undergoes no change during the period in which betaine is administered, but there is a continuous increase in the amount of nitrogen present as compounds which cannot be identified. In the first few days, betaine acts as a mild diuretic and produces an increase of nitrogen in the faeces, but does not itself occur in the latter. The authors conclude that betaine plays a definite part in the animal organism. Small proportions of betaine may be detected in sheep's urine, but no trace of betaine could be found in the urine of a cow fed daily with molasses.

T. H. P.

Nuclein Bases produced during the Autofermentation of Pancreas. MARTIN SCHENCK (*Zeit. physiol. Chem.*, 1905, 43, 406—409. Compare Schittenhelm, *Abstr.*, 1904, ii, 752, and this vol., i, 108; Jones and Partridge, *Abstr.*, 1904, ii, 838; Levene, *Abstr.*, 1904, ii, 828).—Finely-divided fresh pancreatic glands were allowed to undergo autofermentation in the presence of chloroform water, and after removal of tyrosine, histidine, and arginine the purine bases were isolated by Krüger and Salomon's method. The only bases obtained were guanine and hypoxanthine; xanthine and adenine could not be isolated, and if formed at all were only present in minute quantities. These results can be explained on the supposition that adenase and guanase are two distinct ferments, and that in the extracts examined guanase was not present.

J. J. S.

The Kinetics of Tryptic Action. WILLIAM M. BAYLISS (*Arch. Sci. Biol. St. Petersburg*, 1904, 11, *Suppl.* 281—297).—The electrical conductivity method was the one mainly employed. The typical curve of the velocity of trypsin action differs from a logarithmic curve in that it gradually falls away from such a curve, owing to the retarding action of the products of cleavage, especially amino-acids. The chief cause of increase of conductivity during digestion is probably the splitting off of inorganic constituents, and in the case of caseinogen the formation of inorganic phosphates. Amino-acids also have a slight action in this direction. The existence of a weak proteolytic enzyme in unactivated juice and of anti-trypsin in serum and egg-white is confirmed. There is some evidence of reversible action on the part of trypsin.

W. D. H.

Autolysis. II. The Influence of the Thyroid. SAMUEL B. SCHRYVER (*J. Physiol.*, 1905, 32, 159—170).—The livers of thyroid-fed animals show a greater autolysis after 24 hours than those of non-thyroid-fed control animals. But if the preliminary thyroid feeding lasts more than eight days, the reverse occurs. Thyroid feeding leads to excessive oxidation and burning up of fat, and so contrasts with phosphorus poisoning, where oxidation is lessened and fat accumulates. A full explanation of the action of the thyroid, whether on the tissues or on the autolytic enzymes or on substances which inhibit the enzyme action, is still wanting.

W. D. H.

Inactive Arginine. E. PROVAN CATHCART (*Proc. Physiol. Soc.*, 1904—1905, xv; *J. Physiol.*, 32).—In “urotryptic” digestion of fibrin, the arginine fraction was obtained in crystalline form and was found to be inactive. There is no sharp melting point, but decomposition begins at 210°. The melting point of the active form is 175°. Kutscher obtained the inactive form from a digestion of fibrin with pancreas, or by the treatment of the active form with sulphuric acid.

W. D. H.

Carbohydrate Combustion. III. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1905, 43, 547).—Polemical against Claus and Embden (this vol., ii, 179). This failure to confirm the author's results is attributed to the use of physiological salt solution, which is stated not to be an indifferent reagent like water, but to inhibit ferment action.

W. D. H.

Relation of Cystin to Sulphur Metabolism. C. H. ROTHERA (*J. Physiol.*, 1905, 32, 175—182).—Cystin prepared both from hair and from calculi, when given by the mouth in man, is completely oxidised to sulphate, and appears quantitatively as such in the urine. Cholic acid does not diminish this excretion of sulphates in the urine, as it might if cystin were converted into taurocholate. The two forms of cystin used are believed to be identical. Attempts to get the liver to oxidise cystin to sulphate failed. During the preparation of cystin, a purple coloration was observed with ferric chloride and ammonia; it is attributed to cystein, in which, therefore, an α -thiol-lactic acid nucleus is present.

W. D. H.

Metabolism of Arginine. WILLIAM H. THOMPSON (*J. Physiol.*, 1905, 32, 137—146).—From three experiments on dogs, the following conclusions are drawn. Feeding with arginine chloride or carbonate increases the nitrogen of the urine; of the nitrogen so given, from 73 to 96 per cent. reappears as urea. In the body, therefore, ornithine is either not formed or is largely converted into urea. If the arginine is given hypodermically, more nitrogen is excreted than is contained in the arginine; consequently arginine increases nitrogenous metabolism. In one experiment, glycosuria occurred; the cause of this is not clear.

W. D. H.

A Theory of Protein-metabolism. OTTO FOLIN (*Amer. J. Physiol.*, 1905, 13, 117—138. Compare this vol., ii, 183).—This is a continuation of the line of argument started by the examination of the urine. The laws governing the composition of the urine are the effects of more fundamental laws governing proteid-katabolism. Voit's theory states that katabolism occurs only in the "circulating proteid." The small amount of living protoplasm which dies is at first dissolved and is so added to the circulating proteid. Pflüger, on the other hand, believes that all proteid is first transformed into living material before katabolism occurs. Schöndorff's experiments in support of this view are inconclusive and can be otherwise interpreted. The chief evidence in favour of Voit's theory is the fact that large quantities of food proteid are katabolised in so short a time. The view taken in this paper is that neither of the two extreme views is correct. Nitrogenous katabolism is of two kinds. One is inconstant and immediate, varies with the food, and leads to the formation of urea, inorganic sulphates, but not of creatinine or "neutral sulphur." The other is smaller in amount, constant in quantity, and is largely represented by creatinine, neutral sulphur, and, to a less extent, by uric acid and ethereal sulphates, and possibly a certain amount of urea. The latter form of metabolism may be termed tissue or endogenous metabolism, whilst the other is exogenous. Endogenous metabolism sets a limit to the lowest level of nitrogenous equilibrium attainable. The proteid sufficient to maintain endogenous katabolism is indispensable; whether the amount exogenously katabolised can be entirely dispensed with is at present questionable, but there is evidence to show that it can largely be replaced by non-nitrogenous food; the nitrogen is easily split off by hydrolysis without oxidation, and thus a non-nitrogenous residue remains available for calorific processes. Urea is absent from the muscles, and its representative creatine is eliminated, not as urea, but as creatinine. The katabolism that terminates in urea formation is not of such fundamental importance as that which leads to the elimination of creatinine. The formation of ammonia and amino-acids which occurs so largely in the intestine, owing to tryptic and ereptic activity, is probably a preliminary means of getting rid of the excess of nitrogen taken in. The evidence that these simple materials are synthesised into tissue-proteids is certainly inconclusive and largely teleological; the formation of urea direct from them by the liver is more probable. The hypothesis that the organism uses proteid if it

can get it, even when fats and carbohydrates are abundant, is also considered to be an unproved assumption. The well-established fact that the organism tends to maintain nitrogenous equilibrium within tremendously wide limits is inconsistent with the teleological argument of albumin formation. An extensive formation of Voit's circulating proteid to be followed immediately by decomposition into urea is quite as improbable as the corresponding formation and decomposition of Pflüger's organised protoplasm.

The organism requires in its food only the small amount of nitrogen necessary for endogenous metabolism; the nitrogen of the extra proteid is unnecessary, and the organism has at hand an active mechanism for immediately casting it out.

In carnivorous animals, the uncertainty of the food supply has led to the development of a capacity to store a proteid reserve in the form of increased muscle substance, but in man this does not exist. Still, that does not mean that the human organism can only replace lost muscle tissue slowly and with difficulty, for in convalescence from disease, recovery of weight is astonishingly rapid. The 118 grams per diem of proteid in standard diets is most excessive, and should largely be replaced by carbohydrates. The argument that most people take as much is of no real value, and might be equally well applied to the daily use of wine. The argument that nitrogenous equilibrium cannot be maintained for long periods on less has been disproved, notably by the recent work of Chittenden (this vol., ii, 179). In disease, where the presence of excess of waste is likely to be more harmful than in health, it is recommended that the intake of nitrogen should be limited to the level of the endogenous requirement (3 to 4 grams daily). The fact that muscular work does not increase proteid katabolism is remarkable if current views on the nature of that katabolism are correct, but it becomes intelligible if proteid katabolism, in so far as its nitrogen is concerned, is independent of the oxidations which give rise to heat or to the energy that is converted into work. Whether severe work will have an effect on the endogenous metabolism cannot be shown by investigating urea excretion; determinations of creatinine and neutral sulphur are necessary for a study of that question. W. D. H.

Gastric Digestion. PAUL GRÜTZNER (*Pflüger's Archiv*, 1905, 106, 463—522).—A brief *résumé* of the work done on the mechanism of gastric digestion from the time of Beaumont to the work of Cannon is followed by an account of numerous experiments on animals from the frog upwards. Some attention is directed to the amount of pepsin and acid in the two principal districts of the stomach at varying intervals after digestion has started, but the paper in the main deals with the mechanical aspect of the problem. The pyloric region is the great portion for active digestion and peristalsis; the cardiac half is at first, at any rate, in a resting condition when little or no admixture with gastric juice occurs, but when salivary digestion is unimpeded. The two regions are frequently separated by a band of contraction.

W. D. H.

Effect of Salt Solutions on Cilia. SAMUEL S. MAXWELL (*Amer. J. Physiol.*, 1905, 13, 154—170).—One-eighth mol-solutions of the

chlorides of lithium, ammonium, sodium, potassium, magnesium, calcium, strontium, and barium were employed on the ciliated epithelium of the frog's gullet. Sodium chloride is the most favourable to the prolonged life of the cells and the working power of the cilia. The action of the salts bears no direct relation to valency of the cations or to molecular weight. In general, salts of higher solution-tension are more favourable than those of lower, but the agreement is not exact.

W. D. H.

Distribution of Potassium in Animal and Vegetable Cells.

ARCHIBALD B. MACALLUM (*J. Physiol.*, 1905, **32**, 95—128).—For the microchemical detection of potassium, the following solution is recommended: cobalt nitrite 20 grams, sodium nitrite 35 grams, 10 c.c. glacial acetic acid, and 100 c.c. water. If potassium is abundant the hexanitrite of cobalt and potassium is precipitated as yellow crystals. If the amount of potassium is small, there is only a yellow colour; this is turned black (cobalt sulphide) on the addition of ammonium sulphide. The black coloration forms a very delicate test. The results of the examination of various animal and vegetable cells are described with coloured illustrations. Among these, the following may be mentioned: potassium is found in cell protoplasm, but more abundantly in intercellular material; in striped muscle it is limited to the dim bands, and in pancreatic cells to the granular zone. It is absent from all nuclei and from nerve cells. In nerve fibres, it occurs in curious patches external to the axis, especially at the nodes.

W. D. H.

Influence of Salts on the Resting Current of Frog's Muscle.

RUDOLF HÜBER (*Pflüger's Archiv*, 1905, **106**, 599—635).—The membrane of muscle fibres, unlike that of blood corpuscles, is in the main impermeable to either anions or cations, even in the presence of carbon dioxide. But a special permeability to potassium ions exists. The cations of the alkalis are arranged in order according to their capability of exciting the ordinary current of rest; the anions may be arranged according to their power to excite a current in the opposite direction. The heavy metals and hydrogen ions excite the resting current; the chlorides of the alkaline earths do not, but produce a sort of coagulation of the membrane. All salts that call forth a resting current stimulate muscle to action.

W. D. H.

Action of Potassium and Sodium on the Indirect Excitability of Muscle.

FRANK S. LOCKE (*Proc. Physiol. Soc.*, 1904—1905, xxii; *J. Physiol.*, **32**).—Overton's statement that the addition of potassium salts to sodium chloride solution hastens the disappearance of indirect excitability is confirmed. This, however, is different from a curare action, which consists in the replacement of tetanus on faradisation by weaker and weaker initial contractions.

W. D. H.

Muscle of Octopods. MARTIN HENZE (*Zeit. physiol. Chem.*, 1905, **43**, 477—493).—Octopus muscle contains 77.3 per cent. of water and 13.13 per cent. of nitrogen. It is characterised by its richness in taurine. Creatine, creatinine, urea, hexon bases, amino-acids, and glycogen are all absent. Small quantities of hypoxanthine are present,

and another base not yet identified. Sarcosolactic acid is often absent, and small quantities of fermentation lactic acid are found. The amount of inorganic salts is greater than in vertebrate muscle, and salts of potassium are more abundant than those of sodium. W. D. H.

Influence of Meat Diet on the Thyroid and Parathyroids
CHALMERS WATSON (*Proc. Physiol. Soc.*, 1904—1905, xvi—xvii; *J. Physiol.*, 32; *Brit. Med. J.*, 1905, Jan. 21; *Lancet*, 1905, Feb. 11. Compare Abstr., 1904, ii, 426).—In fowls, excessive meat diet leads to hypertrophy of the thyroid and parathyroid glands. In rats, the effect is usually also fatal; the parathyroids are not affected, but the thyroid generally shows histological changes, which indicate exhaustion of its functions. The question is related to that of gout, and thyroid medication frequently tends to permanent relief. The theory that uric acid is the cause of gout needs revision; the disease is probably infective *via* the alimentary tract; uric acid merely gives the inflammation its specific character. W. D. H.

Oxidation of Nucleic Acid with Calcium Permanganate. Oxidation and Synthetic Formation of Uric Acid in Extracts of Ox Liver. The Source of Endogenous Purine in Man and Mammals. RICHARD BURIAN (*Zeit. physiol. Chem.*, 1905, 43, 494—496, 497—531, 532—546. Compare Abstr., 1903, ii, 313, 317; 1904, i, 354, 358, 956).—Kutscher and Seemann were unable to obtain uric acid by oxidising nucleic acid; they therefore doubt its origin from purine bases. This is because calcium permanganate destroys uric acid.

The presence of oxygen is necessary to obtain in liver extract uric acid from the purine bases it contains, or that are added to it. The uric acid found comes almost exclusively from xanthine, and is due to a ferment, xanthine-oxydase. Liver extracts also destroy to some extent uric acid when formed. No evidence of a synthetical formation of uric acid was discoverable.

An analogy is drawn between endogenous and exogenous purine and creatinine in the urine. The formation of creatine and hypoxanthine in muscle is similar, but nuclein- or nucleo-proteid play no part in the origin of either. Muscular hypoxanthine is the main source of endogenous purine in the urine, and its transformation into uric acid is the work of an oxydase. W. D. H.

Inter-relationship of Calcium and Magnesium Excretion. JOHN MALCOLM (*J. Physiol.*, 1905, 32, 183—190).—Evidence is adduced to show that the ingestion of soluble magnesium salts causes a loss of calcium in adult animals, and hinders its deposition in young growing animals. Soluble calcium salts do not affect the excretion of magnesium in a similar way. W. D. H.

Scatoxyl and the Origin of Scatolic Pigments. LOUIS C. MAILLARD (*J. Pharm. Chim.*, 1905, 21, 187—190).—Largely polemical. A reply to Porcher and Hervieux (this vol., ii, 187). L. DE K.

Analysis of an Intestinal Gravel. CHAPUS (*J. Pharm. Chim.*, 1905, 21, 191—192).—The matter contained 23·5 per cent. of mineral matter, mainly consisting of calcium triphosphate and magnesium-ammonium phosphate; carbonates were absent. The organic and volatile portion contained proteids 8·15, fatty matter 3·57, free stercobilin 3·37, stercobilin combined with calcium 11·63, cellulose, ammonium salts, &c. Biliary colouring matter could not be detected.

L. DE K.

Excretion of Water in Typhoid Fever. TORALD SOLLMANN and J. A. HOFMANN (*Amer. J. Med. Sci.*, February, 1905).—The free administration of water to typhoid patients causes a large polyuria (3 to 9 litres daily). The percentage of chlorides and the total molecular concentration are much below the normal, but the total excretion of dissolved molecules exceeds that in ordinary typhoid cases. The excretion of water and chlorides is nearly parallel to the income, the kidney function being unimpaired. The amount of urine is influenced by the perspiration, and to a less extent by catharsis. Temperature does not directly influence the diuresis. Diuretics, slight nephritis, and calcium chloride have no effect. The excretion of water and chlorides in typhoid fever appears to obey the same laws as in health; there is, however, a greater tendency to chloride retention in the fever, but this is greatly diminished by polyuria. Prolonged restriction of the chloride income produces no deleterious effect; the patients do not develop "salt hunger."

W. D. H.

The Composition of Caseous Deposits in Tubercle. E. SCHMOLL (*Chem. Centr.*, 1905, i, 280—281; from *Arch. klin. Med.*, 81, 163—180).—The chief material in tubercular caseous deposits is a coagulated proteid which in composition approaches albumin, globulin, and also fibrin. Any characteristic constituents of cell-nuclei are not detectable. Cholesterol and lecithin are also present.

W. D. H.

Treatment of Trypanosomiasis by Arsenious Acid and "Trypanroth." A. LAVERAN (*Compt. rend.*, 1905, 140, 287—291).—Infections with *Trypanosoma gambiense* are in certain species of animals curable by successive treatment with arsenious acid and "trypanroth." The efficacious doses border on the toxic, so the dose advisable for cases in man is difficult to determine.

W. D. H.

Toxicity of Sea Water on Fresh-water Animals. WOLFGANG OSTWALD (*Pflüger's Archiv*, 1905, 106, 568—598).—Experiments with sea water in various degrees of dilution on *Gammarus pulex* are represented by curves of toxicity; the males are more resistant than the females. A large number of observations are also recorded in regard to the individual salts, and conclusions similar to those of Ringer, van't Hoff, and Loeb are arrived at.

W. D. H.

Physical Chemistry of Anæsthesia. BENJAMIN MOORE and HERBERT E. ROAF (*Thompson, Yates, and Johnston Lab. Report, Liverpool*, 1905, 6, 151—194).—A full account of researches previously published (*Abstr.*, 1904, ii, 501).

W. D. H.

Effect of Chloroform and Ether on Renal Activity.

WILLIAM H. THOMPSON (*Proc. Physiol. Soc.*, 1904—1905, xxi; *J. Physiol.*, 32).—On the quantity of urine and of nitrogen, the effects of both anæsthetics are very variable. An increase in excretion of chlorides always occurred, especially with chloroform. W. D. H.

Relation of Enterokinase to Trypsin. WILLIAM M. BAYLISS

and ERNEST H. STARLING (*J. Physiol.*, 1905, 32, 129—136).—Normal rabbit's serum, besides its known antitryptic qualities, sometimes has the power of neutralising or destroying enterokinase. If this power is absent, it may be evoked by repeated injection of enterokinase. The production of antikinase does not increase the antitryptic power of the serum. Injection of trypsinogen does not produce any anti-trypsinogen in the serum. The antitryptic power of serum is therefore not due, as stated by Delezenne, to the presence of antikinase. There is also no evidence that a solution of trypsin is equivalent to a combination of kinase and trypsinogen. Trypsin is a new substance produced from trypsinogen by the ferment-like action of enterokinase. The enterokinase does not appear to be essential to, or take any part in, the proteolytic activities of trypsin. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Biological and Biochemical Studies on Milk. C. J. KONING (*Milchw. Zentr.*, 1905, i, 49—68).—A series of experiments is described on the number of bacteria present in fresh milk and in the same milk after 6, 18, 30, 42 or more hours. The results generally show a fall in the number in the early periods, followed by a rapid rise.

N. H. J. M.

Formation of Volatile Alkaloids in Sterilised Milk by *Bacillus Nobilis*. Occurrence of such Compounds in Emmen-thaler Cheese. LEOPOLD ADAMETZ and T. CHSZASZEZ (*Milchw. Zentr.*, 1905, i, 78—80).—Cultures of *Bacillus nobilis* in milk which had been kept 22 months yielded, when distilled, a basic substance *tyrothrixin*, which was obtained from the distillate by extraction with ether. It is a white, crystalline substance having a sharp, characteristic odour, sparingly soluble in water, insoluble in sodium and potassium hydroxides, readily soluble in ether, alcohol, or dilute acids. When treated with ammonia, it forms needles 1—2 mm. long. Phosphomolybdic acid produces a canary-coloured precipitate; phosphotungstic acid a white precipitate readily soluble in an excess. Potassium-mercury iodide yields a precipitate of long, canary-coloured needles. Gold chloride gives a lemon-coloured precipitate which, however, soon decomposes with liberation of gold. Concentrated solutions of picric

acid yield an abundant yellow precipitate. The substance is volatile at the ordinary temperature; a few milligrams kept under a large glass shade almost completely disappear in 36 hours.

The same compound occurs in Emmenthaler cheese.

N. H. J. M.

Fusel Oil. HANS H. PRINGSHEIM (*Ber.*, 1905, 38, 486—487. Compare Emmerling, *Abstr.*, 1904, ii, 834).—A red bacillus has been isolated from American potatoes, a pure culture of which ferments potatoes yielding hydrogen, carbon dioxide, and an oil with a strong odour of amyl alcohol and boiling at 112—130°. Distinct spore formation has been observed, and these spores are not destroyed when heated for 10 minutes at 80°. Ten per cent. gelatin at 22° is readily liquefied by the organism. It is not at all certain that the fusel oil obtained in alcoholic fermentation is due to this organism, since its growth and fermentative action are prevented by the addition of 10 per cent. of ethyl alcohol, whilst the formation of fusel oil takes place chiefly towards the close of the alcoholic fermentation, when more than 10 per cent. of alcohol is already present.

J. J. S.

Resting Yeast in Moist and Pressed Conditions. Action of Foreign Organisms on the Behaviour and Duration of Life of Yeast Cells. WILHELM HENNEBERG (*Chem. Centr.*, 1905, i, 688; from *Zeits. Spiritusind.*, 28, 1—2, 12, 23, 30, 39, and 48. Compare *Abstr.*, 1903, ii, 168).—The duration of life of yeast is shown to depend on race, temperature, moisture, aëration, and the nature of the infection. Acetic bacteria are the most injurious, and some lactic acid bacteria and *Penicillium* are also injurious. *Oidium lactis* is beneficial, whilst *Pediococcus*, wild yeast, and putrefactive bacteria have no particular effect. Slow drying is favourable, quick drying injurious.

To avoid a considerable infection of yeast, the mash is heated to at least 68°. *Mucor*, *Penicillium*, *Oidium*, putrefactive bacteria, and hay bacilli grow spontaneously in yeast.

N. H. J. M.

Chemical Reactions occurring during Alcoholic Fermentation. EDUARD BUCHNER and JACOB MEISENHEIMER (*Ber.*, 1905, 38, 620—630. Compare *Abstr.*, 1904, ii, 199).—The work of other authors bearing on the formation of lactic acid from dextrose and of alcohol from lactic acid is fully discussed. Small quantities of alcohol are conveniently detected by means of *p*-nitrobenzoyl chloride, and this has been made use of to prove that small quantities of alcohol are formed by boiling invert sugar with sodium hydroxide.

Harriot has shown (*Abstr.*, 1886, 224) that calcium lactate when distilled with lime forms large quantities of alcohol; part of this is now proved to be isopropyl alcohol. isoPropyl *p*-nitrobenzoate crystallises in light yellow prisms melting at 111°. A further series of experiments is adduced to prove that lactic acid is a product of the fermentation of dextrose by pressed yeasts; in the main, however, as much lactic acid is formed in the absence as in the presence of the dextrose.

E. F. A.

Zymase and Alcoholic Fermentation. ARTHUR HARDEN (*J. Inst. Brewing*, 1905, 11, 2—13).—A *résumé* of the properties of yeast juice. The paper also includes an account of some of the work carried out by the author (Harden, *Abstr.*, 1903, ii, 319; Harden and Young, *Abstr.*, 1904, i, 543; this vol., ii, 109). A. McK.

Lecithin in Wine. ANGIOLO FUNARO and I. BARBONI (*Chem. Centr.*, 1905, i, 552; from *Staz. sperim. agrar. ital.*, 1904, 37, 881—897).—Seventeen different samples of wine have been examined for lecithin, and the conclusion is drawn that this is a normal constituent. On the average, 260 mg. of lecithin per litre are present in Tuscan wines. Red wines appear to contain more than white wines. The source of the lecithin is not only the grape seeds, but also the fleshy part of the fruit. There is no connection between the amounts of phosphorus and of lecithin or of alcohol present in a wine. The lecithin is not destroyed when the wine is heated (compare Rosenstiehl, *Abstr.*, 1904, ii, 688; Weirich and Ortlieb, 1904, ii, 304).

H. M. D.

Composition of Wine Brandies. XAVIER ROCQUES (*Compt. rend.*, 1905, 140, 511—512).—The brandies of the Charente district contain all the higher alcohols, a large proportion of the aldehydes and esters, and only a very small proportion of the acids of the wines from which they are distilled. The furfuraldehyde, of which traces only exist in the wine, is formed during the process of distillation when the heating is prolonged; thus, a wine which on rapid distillation from a glass vessel gave only 0·3 gram of furfuraldehyde per 100 litres of pure alcohol, gave 4·4 grams when distilled slowly from a copper retort. A summary of the results of analyses of twenty-two specimens of brandy is given in the following table (the results are expressed in grams per 100 litres of alcohol):

	Maximum.	Minimum.	Mean.
Acids	37·7	10·0	18·6
Aldehydes	33·5	3·8	14·6
Esters	213·0	65·9	121·0
Higher alcohols.....	292·4	115·0	211·4
Furfuraldehyde	4·4	0·2	2·4
Total, or non-alcoholic coefficient	475·6	280·1	367·5
Higher alcohols and esters	429·0	235·2	333·9
Ratio, $\frac{\text{higher alcohols}}{\text{esters}}$	4·4	0·7	1·9

M. A. W.

Assimilation outside the Organism. CH. BERNARD (*Compt. rend.*, 1905, 140, 509—511).—The opinion has been expressed that the decomposition of carbon dioxide by plants is the result of ferment action. Whilst not denying the possibility, the author has found in repeating and extending former experiments that no evolution of oxygen occurs in sunlight as the result of mixing chlorophyll and extracts of plant tissues. If bacterial decomposition sets in, gaseous products are naturally obtained, but not oxygen. W. D. H.

Nutrition of Green Plants with Nitrogen. O. TREBOUX (*Chem. Centr.*, 1905, i, 619; from *Ber. deut. bot. Ges.*, 22, 570—572).—Nitrogen as nitrites is generally satisfactory as a source of nitrogen in alkaline solutions, but poisonous in acid solutions. The poisonous action of nitrites is only observed when a certain concentration is reached; this concentration is only slightly lower than in the case of ammonium salts. Nitrates have the same, or a greater, nutritive value, whilst ammonium salts are still better. Amino-acids and amides are suitable for lower green plants, but for higher plants the value of amino-acids is much less. Ammonium salts of the corresponding organic acids are generally better than the amino-acids. It is more probable that asparagine and other amino-compounds are decomposed by enzymes with liberation of ammonia than that they are directly employed in the production of proteids. Nitrogen assimilation is independent of chlorophyll. All the plants grew better with heterotrophic than with autotrophic carbon. Mosses can grow without calcium.

Nitrogen as ammonium salts seems to be the best form of nitrogen for chlorophyllous plants, and the intervention of nitrite and nitrate bacteria is unnecessary.

N. H. J. M.

Leucine and Tyrosine as Sources of Nitrogen for Plants. L. LUTZ (*Compt. rend.*, 1905, 140, 380—382).—Both leucine and tyrosine were assimilated by *Cucumis vulgaris* and by *Aspergillus niger*, *Aspergillus repens*, and *Penicillium glaucum*.

N. H. J. M.

Consumption of Odoriferous Substances in Etiolated Plants. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Compt. rend.*, 1905, 140, 455—457. Compare Abstr., 1903, ii, 172, 607).—When kept in the dark, plants are able to utilise the essential oil, and especially terpene compounds. It had previously been observed that etiolated plants contained less essential oil than normal plants.

N. H. J. M.

Composition and Signification of Aleurone Grains. SWIGEL POSTERNAK (*Compt. rend.*, 1905, 140, 322—324).—The presence of anhydro-oxymethylenediphosphoric acid (phytine) in aleurone grains has already been observed (Abstr., 1903, ii, 607). An organic acid was also found in the grains of the spruce-fir. The following amounts of total nitrogen and mineral substances were found in the aleurone grains of (1) spruce fir, (2) sunflower, (3) hemp, and (4) white lupin:

	N.	K.	Ca.	Mg.	Fe.	Mn.	P.	S.	Si.
1.	12·97	2·50	0·37	1·25	0·09	0·25	2·67	0·64	0·35
2.	10·22	2·29	0·32	1·46	0·05	trace	2·78	0·64	0·24
3.	12·88	2·71	0·27	1·67	0·03	trace	3·83	0·81	0·36
4.	10·70	—	0·11	0·28	—	0·11	0·61	—	0·01

Sodium and chlorine were not found.

N. H. J. M.

Amount of Hydrogen Cyanide in the Seeds of *Gynocardia Odorata*. MAURITS GRESHOFF (*Chem. Centr.*, 1905, i, 683; from *Pharm. Weekbl.*, 42, 102—105).—The pressed seeds yielded 40

per cent. of oil soluble in light petroleum, which, when kept for 24 hours in a closed vessel with water, yielded 0.92 per cent. of its weight of hydrogen cyanide. The fresh seeds probably contain more than 1 per cent. of hydrogen cyanide (compare Power and Gornall, *Proc.*, 1904, 20, 135).
N. H. J. M.

Oil from the Seeds of *Calophyllum Inophyllum*. GEORG FENDLER (*Chem. Centr.*, 1905, i, 463; from *Apoth. Zeit.*, 20, 6—8).—The seeds contained 22.8—31.5 H₂O and 50.5—55 oil per cent. The oil has a yellowish-green colour, an odour resembling fenugreek, a bitter taste, and, on keeping, fatty glycerides are deposited. It solidifies at 3°, melts again at 8°, and has a sp. gr. 0.9428 at 15°, Reichert-Meissl number 0.13, saponification number 196.0, acid number 28.45, iodine number 92.8, refractometer number 76 at 40°; it contains 0.25 per cent. of unsaponifiable matter. The increase in weight due to oxygen absorption, when measured by Livache's method, amounted to 0.25, 0.71, 1.32, and 1.84 per cent. after 18, 40, 64, and 136 hours. Treatment with 5 per cent. soda solution removes the resinous constituents. The purified oil solidifies at 4°, melts again at 8°, and has Reichert-Meissl number 0.18, saponification number 191, iodine number 86. The fatty acids of the oil are chiefly palmitic, stearic, and oleic.
H. M. D.

Urea [in Fungi]. RUDOLF GAZE (*Arch. Pharm.*, 1905, 243, 78—79).—Urea (carbamide) was isolated from the fungus *Lycoperdon Bovista* (M. Bamberger and Landsiedl, *Abstr.*, 1903, ii, 567), growing in the neighbourhood of Gersfeld (Rhön), in about equal amount from mature and from immature specimens.

From *Lycoperdon cervinum*, much mannitol could be isolated, but no urea.
C. F. B.

Barley. EUGEN PRIOR (*Chem. Centr.*, 1905, i, 682; from *Allgem. Zeit. Brauerei Malzfabr.*, 1904. Compare *Abstr.*, 1902, ii, 479).—The amount of water in 49 barleys varied from 10 to 13 per cent., the proteids from 9 to 14 per cent. The nitrogen question can only be settled when the nature as well as the amount of the nitrogenous matters in barley and malt is made clear, and when it is known which substances are useful or injurious for malting.
N. H. J. M.

Pot Experiments [on the Action of Lime and Magnesia] on Barley. RICHARD ULBRICHT (*Landw. Versuchs-Stat.*, 1905, 61, 357—369. Compare *Abstr.*, 1902, ii, 581).—Application of much dolomite in the spring raised the yield of grain, whilst application in the winter diminished the yield. With a mixture of burnt lime and burnt magnesite, the effect is reversed.
N. H. J. M.

Injurious Action of Crude Potassium Salts on Potatoes. H. SÜCHTING (*Landw. Versuchs-Stat.*, 1905, 61, 397—449).—Sodium carbonate does not injure potatoes when the amount is 3.4 grams (of Na₂O) in 19 kilos. of soil. Potatoes which contained the most sodium at the most active period of vegetation gave the highest yields. The

injurious effect of sodium chloride is therefore due to the chlorine. Manuring with sodium salts results in a diminished assimilation of potassium.

During the vegetative period, sodium is distributed equally through the plants; towards the end of the vegetative period, it accumulates in the leaves. When sodium chloride is employed, the excess of chlorine in the leaves during growth migrates later on, in part, to the tubers. Sodium chloride was not found to give rise to a greater retention of potassium in the leaves.

N. H. J. M.

Estimation of the Fertility and Manurial Requirements of Soils. JOSEF KÖNIG (*Landw. Versuchs-Stat.*, 1905, **61**, 371—396).—Determinations of the potassium and phosphoric acid of ten different soils, soluble in cold hydrochloric acid of sp. gr. 1.15 and in 1 and 2 per cent. citric acid solutions, gave irregular results, from which the conclusion is drawn that the nutritive constituents occur in very different forms. Further experiments, in which different soils were treated with increasing amounts of soluble manures (potassium and phosphoric acid) and then extracted with 2 per cent. citric acid, showed that some of the manure was retained by the soil.

Comparing the results of pot experiments (with barley) with the amounts of soil constituents dissolved by 2 per cent. citric acid, it was found that the citric acid dissolved far more potassium and phosphoric acid than was taken up by the plants.

N. H. J. M.

Use of Peat for the Transformation of Calcium Cyanamide into Ammoniacal Compounds. R. PEROTTI (*Atti R. Accad. Lincei*, 1905, [v], **14**, i, 174—177).—When calcium cyanamide (Kalkstickstoff) is applied as a manure, the vegetation is first of all injuriously affected, but after a time it recovers and grows with increased vigour. The author shows that this is due to hydrolysis of the calcium cyanamide by the soil with the formation of ammonium salts. This hydrolysis is readily effected if the calcium cyanamide is mixed with peat and water. It is suggested that the solution of ammonium salts thus obtained should be used for the hydrolysis of a fresh quantity of calcium cyanamide and that this process be repeated, the final mixture then being very rich in nitrogen.

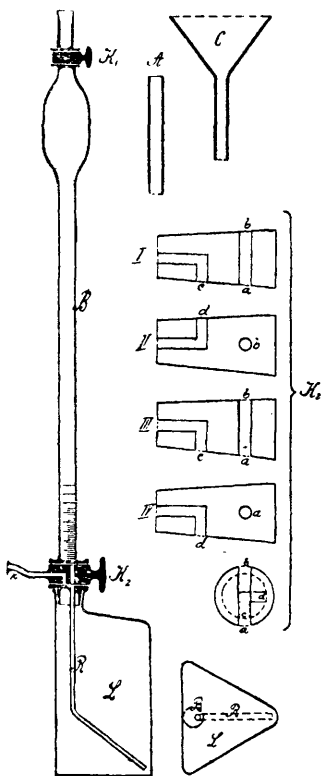
T. H. P.

Analytical Chemistry.

Apparatus for Testing Gases. RUDOLF FIEBER (*Chem. Zeit.*, 1905, 29, 80).—A compact apparatus, consisting of a gas-burette and four absorption vessels, for the details of which reference must be made to the original paper

L. DE K.

Apparatus for Gas Analysis. V. KARLÍK (*Zeit. Zuckerind. Böhm.*, 1905, 29, 233—235).—The flask, *L*, contains the absorbent liquid, and ground into its neck is the burette, *B*, which has a content of about 50 c.c. and is divided into 100 parts, the lowest 40 of which are numbered when the apparatus is to be used for the examination of the saturation gases of sugar factories. The cock, *K*₁, allows the burette to be connected with the space containing the gas to be analysed, whilst the three-way tap, *K*₂, permits of connection being made between burette and flask (*via* the bent tube, *R*), burette and air or flask and air. *K*₁ is first opened, *K*₂ put in position *I*, and the absorbent solution poured down the funnel, *C* (with ground tube), through the burette into *L*, and finally passes out by the tube, *r*. The latter is then bent upwards so that the space *ab* is filled with the liquid. *K*₂ is now turned into position *II* and the burette rinsed out with water, which also passes out through *r*. The gas under investigation is now passed through the adapting tube, *A*, into the burette and is allowed to flow through for some time before the tap is shut. Where the gas is not under pressure or small in quantity, it is drawn into the burette by suction. *K*₁ being closed, *K*₂ is brought into position *III* and the apparatus arranged horizontally, so that the bent end of the tube *R* points downwards. Part of the liquid now passes into the burette and the amount of this may be increased by careful blowing down the tube *r*. As absorption of the gas takes place, more and more of the liquid enters the burette, and this goes on until absorption ceases; the end of *R* must always be kept underneath the surface of the liquid so that air cannot pass into the burette. When absorption is complete, the apparatus is so inclined that the surfaces of the liquid in the burette and in the flask are in the same plane, and the cock *K*₂ brought into position *III*, and then into position *IV*. The apparatus is then placed vertically and the burette read off. *K*₁ is then opened and *K*₂ put as in *I*, the liquid then flowing from the burette into the flask *L*; in case *ab* is not filled with the liquid, this is effected by inclining the apparatus. *K*₂ is placed in position *II* and the burette washed out with water, after which the apparatus is ready for a new estimation. The apparatus is made entirely of glass and contains no india-rubber or brass connections.



T. H. P.

Apparatus for estimating Volatile Substances by Loss of Weight. J. LEHN KREIDER (*Amer. J. Sci.*, 1905, 19, 188—190).—The apparatus is made from three test-tubes. One retains its ordinary shape; the second is perforated in the bottom with a hole about 1 centimetre in diameter, and fits tightly in the first tube, so that about one-third its length is in the latter. The third test-tube, which fits loosely into the second, is drawn out at the bottom to a capillary tube and closed at the top by a cork, through which passes a tube provided with an india-rubber cap. The hole in the second tube is lightly packed with cotton-wool and the capillary tube passed through it. This second tube is about half-filled with calcium chloride, which surrounds the capillary tube above the hole. The substance to be examined is weighed out into the first test-tube, whilst the reagent employed to liberate the volatile product is drawn up into the third test-tube, as in a pipette, and held there by replacing the india-rubber cap. After fitting the tubes together, the apparatus is weighed. The cap is then removed, when the reagent flows down the capillary tube on to the substance in the lower tube. The volatile product passes through the cotton-wool and calcium chloride and escapes by the narrow space between the sides of the second and third test-tubes. At the end of the operation, a current of dry air is forced through the apparatus before re-weighing. If necessary, the joint between the first and second test-tubes may be made air-tight by means of a little melted wax. The apparatus is suitable for estimating carbon dioxide in carbonates, nitrogen in ammonium salts and urea, &c.

W. P. S.

Preparation of Volumetric Solutions. EDWARD C. WORDEN and JOHN MOTION (*J. Soc. Chem. Ind.*, 1905, 24, 178—182).—Tables are given showing the specific gravities and corresponding percentage strengths of solutions of sulphuric, hydrochloric, and oxalic acids. The tables show differences of 0.0001 in the specific gravities (or 0.005 per cent. of acid), and the fifth decimal place can be readily interpolated. To prepare a normal solution, 27 c.c. of sulphuric acid of sp. gr. 1.84, 95 c.c. of hydrochloric acid of sp. gr. 1.19, or 63 grams of crystallised oxalic acid are dissolved in water to 1 litre. The specific gravity is carefully taken and the exact strength of solution obtained from the tables. A normal factor may then be calculated for the solution.

W. P. S.

Benzene as Indicator for Iodimetry. B. SCHWEZOFF (*Zeit. anal. Chem.*, 1905, 44, 85—88).—The red colour of a solution of iodine in benzene is visible with quantities of iodine too small to produce a distinct blue with starch paste. Benzene may therefore be substituted for starch in iodimetric titrations. The first appearance of the colour when titrating with iodine is more easily observed than its disappearance when titrating with thiosulphate. The titration must be performed in a well-stoppered bottle and with vigorous shaking.

M. J. S.

Estimation of Perchlorates. MAX DITTRICH and H. BOLLENBACH (*Ber.*, 1905, **38**, 751—752. Compare Lemaitre, *Abstr.*, 1904, ii, 587).—To reduce perchlorates to chlorides, the bottom of a crucible is covered with a layer of sodium nitrite, the sample to be analysed placed on the centre, and a further layer of nitrite added; the mass is then fused and kept so for half an hour at as low a temperature as possible. The perchlorate must not touch the side of the crucible, as otherwise explosions are apt to occur.

The reduction of perchlorates, present in potassium nitrate, on fusion is preceded by the decomposition of the nitrate to nitrite; by adding sodium nitrite, the reduction temperature is lowered, and the risk of loss of chloride is avoided. G. Y.

Estimation of Small Proportions of Bromine and Chlorine in Iodine. ROBERT R. TATLOCK and ROBERT T. THOMSON (*J. Soc. Chem. Ind.*, 1905, **24**, 187—188).—For estimating small quantities of bromine and chlorine in commercial iodine, the following method is given: 10 grams of the sample are treated with 100 c.c. of water and zinc dust is added in small quantities at a time until all the iodine is converted into zinc iodide. Care must be taken that the temperature does not rise appreciably. The solution is now filtered and 7 grams of pure sodium nitrite are added to the filtrate. By carefully acidifying the solution with dilute sulphuric acid, all the iodine is liberated and almost completely precipitated, but no bromine is set free. The iodine is collected on a filter, washed with water, and the last traces removed from the filtrate by shaking the latter with benzene, this being repeated after adding a little more sodium nitrite and sulphuric acid. The bromine and chlorine are then precipitated as silver salts in the presence of nitric acid, collected on a filter, and washed. The silver chloride is extracted from the precipitate by washing the latter on the filter with a solution of 2 grams of silver nitrate and 10 c.c. of ammonia of sp. gr. 0.88 in 90 c.c. of water. The silver bromide remains insoluble and the silver chloride may be reprecipitated from the ammoniacal solution by the addition of nitric acid. The silver bromide precipitate should always be tested qualitatively for bromine.

W. P. S.

New Process for Titrating Iodine. H. HENNECKE (*Chem. Centr.*, 1905, i, 294; from *Pharm. Zeit.*, 1904, **49**, 1095—1096).—A reply to a criticism by Jünger (*Pharm. Zeit.*, **49**, 1040—1041). The author upholds the validity of his process (*ibid.*, 957), and states that iodine chloride, although liberating iodine from any added sodium iodide, does not act on the iodide formed in the reaction.

L. DE K.

Volumetric Estimation of Iodine. H. FRERICHS (*Chem. Centr.*, 1905, i, 561; from *Apoth. Zeit.*, **20**, 13—14).—An adverse criticism of the method proposed by Hennecke (*ibid.*, 1904, ii, 1623).

L. DE K.

Estimation of Sulphur in Coal by Eschka's Process. CARL BENDER (*Zeit. angew. Chem.*, 1905, **18**, 293).—In order to avoid the

influence of the products of combustion of coal gas on the Eschka soda-magnesia mixture, the heating is conducted in a combustion tube open at one end only. L. DE K.

Apparatus for Absorption of Hydrogen Sulphide in Iron and Steel Analysis. N. JENNER (*Zeit. angew. Chem.*, 1905, 18, 292).—A vertical five-bulb apparatus, each bulb holding 10 c.c., supported by a glass foot. The upper bulb is connected with a funnel-shaped glass vessel holding 50 c.c. and provided with a spout. L. DE K.

Evaluation of Sodium Hyposulphite. ARTHUR BINZ and H. BERTRAM (*Zeit. angew. Chem.*, 1905, 18, 168—170).—Ekker's process, titration with potassium ferricyanide with ferrous sulphate as indicator, is recommended (compare Abstr., 1895, ii, 500). L. DE K.

New Process for detecting Ammonia; Application for characterising the Purity of Waters. AUGUSTE TRILLAT and TURCHET (*Compt. rend.*, 1905, 140, 374—376).—When solutions of potassium iodide and an alkali hypochlorite are added to a liquid containing ammonia, an intense black coloration is produced due to the formation of nitrogen iodide, and as the same result is obtained when the iodine mono- or tri-chloride and an alkali are used instead of the above reagents, the reaction may be represented by the following equation: $3\text{ClI} + \text{NH}_3 + 3\text{NaOH} = 3\text{NaCl} + \text{NI}_3 + 3\text{H}_2\text{O}$. The authors find that no compounds of nitrogen other than ammonium salts form nitrogen iodide under these conditions, and as the reaction is not affected by the presence of proteid matter or alkali sulphides, it forms a more convenient colorimetric test for traces of ammonia in potable waters than the ordinary Nessler test. In applying the test, 3 drops of a 10 per cent. solution of potassium iodide and 2 drops of a concentrated solution of alkali hypochlorite (Eau de Javel) are added to 20 or 30 c.c. of the suspected water; the use of excess of the reagents must be avoided, as nitrogen iodide dissolves under these conditions. M. A. W.

Detection of Nitric Acid by the Diphenylamine Reaction. GUSTAV FRERICHS (*Arch. Pharm.*, 1905, 243, 80).—This reaction can be applied in the following manner, even in the presence of substances such as ferric salts, chromates, &c., which themselves produce a blue coloration.

About 10 c.c. of dilute sulphuric acid are poured over the substance in a test-tube, 20 c.c. of ether added, and the whole shaken. Of the ethereal layer, 2—3 c.c. are filtered into a test-tube, and a grain or two of diphenylamine is added, followed by 5—10 c.c. of concentrated sulphuric acid, when a blue coloration appears if the original substance contains a nitrate.

If the ethereal layer is coloured yellow (iodine, bromine, or chromic acid), it is decolorised by shaking it with a little sulphurous acid, and then a portion is filtered and tested as just described. C. F. B.

Gravimetric Estimation of Nitric Acid. MAX BUSCH (*Ber.*, 1905, 38, 861—866).—The very slight solubility of diphenylendoanilo-

dihydrotriazole nitrate in water (this vol., i, 307) makes it possible to precipitate a nitrate quantitatively by means of the base dissolved in 5 per cent. acetic acid; diphenylendoanilodihydrotriazole is sold by Merck under the name "nitron." To precipitate the nitrate to be estimated, 10—12 c.c. of a 10 per cent. acetic acid solution of "nitron" are added to the hot solution (containing about 0.1 gram HNO_3 per 100 c.c.), to which 10 drops of dilute sulphuric acid have been added; the liquid is cooled for $1\frac{1}{2}$ —2 hours at 0° and the precipitate collected on a Neubauer crucible, washed with 10—12 c.c. of ice-cold water, and dried at 110° . The precipitate has the composition $\text{C}_{20}\text{H}_{16}\text{N}_4\cdot\text{HNO}_3$. The presence of small quantities of chlorides and sulphates does not interfere with the accuracy of the method, but bromides (1 in 800), iodides (1 in 20,000), nitrites (1 in 4000), chromates (1 in 6000), chlorates (1 in 4000), and perchlorates (1 in 50,000) are also precipitated by "nitron." Hydrobromic acid should be previously eliminated by means of chlorine, hydriodic acid by means of an iodate, nitrous acid or chromic acid by hydrazine sulphate. "Nitron" may be used as a qualitative test for nitrates in a dilution of 1 : 60,000.

In order to estimate a nitrate in presence of a nitrite, the solution of the salts (0.2 gram of substance in 5—6 c.c. of water) is added to finely powdered hydrazine sulphate, which completely destroys the nitrite; the nitrate is then precipitated by means of "nitron." Very good results are obtained by this method.

W. A. D.

Estimation of Nitric Acid in Waters. FRANZ UTZ (*Chem. Zeit.*, 1905, 29, 177—178).—Frerich's process (Abstr., 1903, ii, 328), evaporation with hydrochloric acid in order to convert the nitrates into chlorides and estimation of the chloride formed, is recommended.

L. DE K.

Detection of Nitrous and Nitric Acids when occurring together and their Approximate Estimation by means of Diphenylamine. PAUL N. RAIKOW (*Chem. Centr.*, 1905, 1, 402—403; from *Oesterr. Chem. Zeit.*, 7, 557—561).—Nitrites act instantaneously on diphenylamine dissolved in sulphuric acid, yielding a violet-blue colour which changes to blue and finally fades. Nitrates act much more slowly, but yield in the end a blue solution. Therefore, by suitably diluting a solution, both acids may be detected by their different behaviour.

If a solution of diphenylamine in phosphoric acid is used, the liquid turns blue, due to the nitrite; in the presence of nitrates, characteristic black spots are also noticed.

An approximate estimation of either acid may be made as follows: 0.2 gram of diphenylamine is dissolved in 100 c.c. of pure sulphuric acid or syrupy phosphoric acid of sp. gr. 1.7, and 0.5 c.c. is put into a flat porcelain dish. One drop of the solution to be tested is allowed to run into the acid and the colour is then noticed. By diluting again and again until the reaction is scarcely obtained, an idea may be gained as to the strength of the nitrite or nitrate by the fact that for the sulphuric acid solution the reaction limit is 0.0003 mg. of

potassium nitrate and 0.00005 mg. of potassium nitrite; in phosphoric acid solution, 2.5 mg. of potassium nitrate, but only 0.00006 mg. of potassium nitrite.

L. DE K.

[Volumetric] Estimation of Phosphoric Acid. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1905, 18, 374—376).—The solution, which should contain about 0.15 gram of phosphoric oxide, is precipitated with magnesium mixture. The precipitate is collected at the pump on a small filter and then washed first with 10 and then again with 5 c.c. of plain water. The error due to the solubility of the triple phosphate in plain water may be neglected. The filter with the precipitate upwards is then put into a beaker, 20 c.c. of water are added, and the phosphate is titrated with $N/10$ hydrochloric acid, using methyl-orange as indicator. A slight excess of acid may be titrated back with $N/10$ sodium hydroxide. Forty c.c. of $N/10$ acid = 0.142 gram of P_2O_5 .

L. DE K.

Electrolytic Estimation of Small Quantities of Arsenic. CARL MAI and H. HURT (*Zeit. Nahr. Genussm.*, 1905, 9, 193—199).—The apparatus employed by the authors consists of a wide U-tube in which the decomposition is carried out and a six bulb absorbing tube. Between these two parts, and connecting them, is placed a tube filled with pumice-stone soaked in alkaline lead solution. The electrodes consist of pure sheet lead. The ends of the U-tube are closed with caoutchouc stoppers, through which pass glass tubes, elongations on the lead plates being cemented in these tubes, so that a plate is suspended in each limb of the U-tube. A safety-tube passes through the cork of the anode limb, whilst the cork of the cathode limb is pierced by the capillary stem of a tapped funnel and the delivery tube of the apparatus. The U-tube is about two-thirds filled with a 12 per cent. sulphuric acid solution, and 10 c.c. of $N/100$ silver nitrate solution are placed in the bulbs of the absorption tube. The current may be obtained direct from the main and should be controlled by a suitable resistance. The solution to be examined is introduced drop by drop from the tapped funnel. Should arsenic be present, the silver solution is darkened, and at the end of 2, or at the most 3 hours, the reduction is completed. The reduced silver is collected on an asbestos filter, washed with a little water, and the excess of silver in the filtrate titrated with $N/100$ thiocyanate solution. One c.c. of $N/100$ silver nitrate solution is equivalent to 0.125 mg. of metallic arsenic. For quantities of less than 0.02 mg., the titration method fails and a colorimetric one must be employed, when 0.001 mg. of arsenic may be estimated and 0.0005 mg. detected. For the detection of minute traces, the absorption tube may be replaced by the combustion tube of a Marsh apparatus and a mirror obtained in the usual way.

The authors state that all organic matter must be destroyed before estimating arsenic in such articles as beer, urine, &c.

W. P. S.

Evaluation of Sodium Peroxide. HERMANN GROSSMANN (*Chem. Zeit.*, 1905, 29, 137—138).—A slight modification of the method recommended by Archbutt, namely, decomposition in the presence of a little cobalt nitrate (Abstr., 1895, ii, 185).

L. DE K.

Employment of Persulphate for Quantitative Separations.

GEORG VON KNORRE (*Zeit. anal. Chem.*, 1905, 44, 88—96).—A reply to Dittrich and Hassel (*Abstr.*, 1904, ii, 679; see also ii, 213). In answer to the objection that the author's failure to separate copper completely from manganese was due to the production of precipitates too large for complete washing, it is shown that these quantities were not larger than are commonly obtained in separations; that the manganese precipitate could easily be collected and washed in filters of 9—11 cm. diameter; that the method employed by Dittrich and Hassel to detect copper in the manganese precipitate was not sufficiently sensitive; that even when working with the small quantity (0.1 gram of Mn_3O_4) prescribed by Dittrich and Hassel, the manganese precipitate still contained weighable quantities (about 2.6 mg.) of cupric oxide; that repeated dissolution and reprecipitation fail to remove the copper completely, and that even when the precipitate had been repeatedly boiled with 2 per cent. nitric acid until the washings were free from copper, it nevertheless retained about 2 per cent. of copper oxide.

M. J. S.

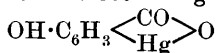
Solubility of Copper Sulphide in Alkali Polysulphides.

V. HASSEIDTER (*Zeit. angew. Chem.*, 1905, 18, 292).—Recent investigations have shown that when copper compounds are fused with sulphur and sodium carbonate, the copper sulphide formed in the reaction is not altogether insoluble in the polysulphide solution. Even copper sulphide formed in the wet way is somewhat soluble in sodium sulphide in the presence of free sulphur.

In order to recover these traces of copper sulphide, the author recommends boiling the solution with cautious addition of sodium sulphite until colourless, sodium monosulphide and thiosulphate being formed which have no solvent action on copper sulphide. L. DE K.

Estimation of Mercury in Organic Mercury Compounds.

ERWIN RUPP and PH. NÖLL (*Arch. Pharm.*, 1905, 243, 1—5).—*Hydrargyrum salicylatum*, to which Dimroth assigns the formula



[CO : OH : Hg = 1 : 2 : 6], is analysed by boiling it gently for one-quarter to half an hour, until the liquid has become colourless, with 5 c.c. of concentrated sulphuric acid and 4 grams of potassium sulphate (free from chloride) in a flask of 150 c.c. capacity, fitted with a cork and glass tube 40—50 cm. long and supported in an inclined position on wire gauze. The tube is then rinsed down into the flask with 5—10 c.c. of concentrated sulphuric acid and removed; 0.1 to 0.2 gram of potassium permanganate is added to the flask, which is then heated for a few seconds until the colour of the permanganate has disappeared. The liquid is allowed to cool, diluted with water to 100 c.c., and allowed to cool completely; 2 c.c. of iron alum solution are added, and the whole is titrated, with continual and vigorous shaking, with *N*/10 thiocyanate solution, 1 c.c. of which = 0.010015 gram Hg, until the brownish-red coloration appears. The condenser tube is to prevent loss of mercurous sulphate by volatilisation; the permanganate to oxidise the mercurous

sulphate formed. Error in these estimations: -0.15 to -0.2 per cent. of the total amount as estimated gravimetrically.

Hydrargyrum succinimidatum, $(C_2H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} N)_2Hg$, can be estimated in the same way. Error: $+0.3$ to $+0.4$ per cent. No reactions being known at present for the detection of this substance, the following are suggested:—(1) Heat 0.1 gram in a dry test-tube with 5 times its weight of zinc dust, and dip into the vapours a deal splint moistened with concentrated hydrochloric acid; the splint is coloured red (pyrrole reaction). (2) Dilute some 1 per cent. solution of the substance with twice its volume of baryta or lime water; a white precipitate is gradually formed, which turns greyish-black when heated or kept (mercuro-amino-compound). C. F. B.

Estimation of Mercury in Organs. O. SCHUMM (*Zeit. anal. Chem.*, 1905, **44**, 73–85).—The organ is minced, mixed with an equal quantity of water and 1 per cent. of chloroform, and in some cases with pepsin and hydrochloric acid, and maintained at 37° until auto-digestion has taken place. The organic matter is then oxidised by heating with hydrochloric acid and potassium chlorate, and the liquid may then at once be electrolysed without expulsion of the last traces of chlorine. The cathode employed is a piece of electrolytic gold foil, 3×1 cm. in area, rolled into a hollow cylinder, to which a fine platinum wire is fused. Electrolysis for 24 hours with an *E.M.F.* of 4 volts precipitates the mercury quantitatively even from 200 c.c. of solution. The cathode is then washed with water, alcohol and ether, dried in a desiccator, and thrust into a tube of hard glass closed at one end. The open end of the tube is drawn out to a capillary, into which the mercury is then distilled. The portion of tube containing the mercury is now cut out with a diamond and weighed. The mercury is then driven off by heat and the tare of the tube ascertained. Should the quantity of mercury be too small for weighing, it may be dissolved from the tube with nitric acid and estimated colorimetrically by adding hydrogen sulphide. Test experiments with 0.3 mg. of mercury gave good results. A trace of sulphur is generally found in the capillary, but the quantity is, as a rule, unweighable. M. J. S.

Estimation of Oxide of Iron in Pyrolusites. H. CORMIMBŒUF (*Ann. Chim. anal.*, 1905, **10**, 51–52).—The powdered ore is ignited in a platinum crucible and then dissolved in hydrochloric acid. The filtrate is partially neutralised with sodium hydroxide and then completely neutralised with pure zinc oxide, an additional 5 grams of which are added. The precipitate is well washed, dissolved in dilute sulphuric acid, and after reducing the iron to the ferrous state with zinc the liquid is titrated with a very weak standard solution of potassium permanganate. L. DE K.

Estimation of Tungsten. GEORG VON KNORRE (*Ber.*, 1905, **38**, 783–789. Compare *Chem. Ind.*, 1905, **28**, 2).—When an excess of benzidine hydrochloride is added to an aqueous solution of sodium

tungstate, a flocculent, amorphous precipitate of benzidine tungstate is deposited. The precipitation is quantitative and the precipitate can be readily filtered if it is thrown down from hot solutions and allowed to cool, or if deposited from cold solutions in the presence of alkali sulphates.

It is advisable to wash the precipitate with dilute benzidine hydrochloride solution and not with water. The precipitating solution contains 20 grams of benzidine and 25 c.c. of concentrated hydrochloric acid per litre, and the solution for washing is made by diluting this with 30—40 times its volume of water. In all precipitations, an excess of some 20—40 per cent. of the hydrochloride solution is employed. The moist precipitate is ignited in a platinum crucible and the tungsten weighed as trioxide.

In many cases, it is necessary to fuse the tungsten compound with sodium carbonate; the fused mass is then dissolved in water, decomposed by the gradual addition of hydrochloric acid until acid to methyl-orange, 10 c.c. of 0.1*N*-sulphuric acid are then added, and the precipitation completed as before.

Ferrous salts do not interfere with the precipitation, but ferric salts must not be present as they oxidise the benzidine; a considerable excess of free acid should also be avoided, as under these conditions the results are low.

When tungsten-steel is dissolved in hydrochloric or dilute sulphuric acid in the absence of atmospheric oxygen, the whole of the tungsten is left undissolved in the metallic state; this is then ignited, first alone, then with sodium carbonate, and precipitated as described previously. It is not advisable to ignite the metallic residue and weigh directly as trioxide, as small amounts of iron are always present. J. J. S.

Tin Analysis. ERNST VICTOR (*Chem. Zeit.*, 1905, **29**, 179—181).—Processes are given for the estimation of the impurities generally occurring in commercial tin.

The direct estimation of tin is effected as follows: the sample is dissolved in hydrochloric acid with addition of potassium chlorate and an aliquot part of the solution is heated with a slight excess of reduced iron or aluminium. The filtrate then contains stannous chloride, which is titrated with standard ferric chloride, using as indicator starch and a solution prepared as follows: 10 grams of potassium iodide are dissolved in 10 c.c. of water and 10 grams of hydriodic acid of sp. gr. 1.5, and 3.3 grams of cuprous iodide are added. This solution should be kept a few days before using it; a few pieces of metallic copper may be added to it, and it should be kept in the dark. L. DE K.

Estimation of Zirconium in Presence of Titanium, especially in Rocks. MAX DITTRICH and R. POHL (*Zeit. anorg. Chem.*, 1905, **43**, 236—241).—The methods generally used for estimating zirconium in presence of titanium are inaccurate when a small amount of one of those elements is present in a mixture containing a relatively large

amount of the other, or when other metals are present in the mixture.

Ammonia was added to a mixture of ferrous ammonium sulphate, titanium nitrate, and zirconium nitrate to which hydrochloric acid and hydrogen peroxide had been added. The resulting precipitate was fused with potassium hydrogen sulphate and the solution of soluble sulphates thus obtained reduced by hydrogen sulphide. To the filtered solution, tartaric acid, ammonia, and ammonium sulphide were added in order to remove the iron completely. After the tartaric acid had been removed, the zirconium and titanium were precipitated together, heated to redness, and weighed. This mixture was then dissolved in potassium persulphate solution and the titanium estimated colorimetrically after the addition of sulphuric acid and hydrogen peroxide.

A mixture of titanium and zirconium salts may also be separated from iron and manganese salts by means of sodium acetate.

A. McK.

Use of Organic Acids for the Precipitation and Separation of Thorium Dioxide from Cerium, Lanthanum, and Didymium Oxides. A. KOLB and H. AHRLE (*Zeit. angew. Chem.*, 1905, 18, 92—93).—Cinnamic, benzoic, and salicylic acids, and especially *m*-nitrobenzoic acid, are suitable for the precipitation of thorium salts. When an aqueous solution of *m*-nitrobenzoic acid is added to a neutral solution of a thorium salt, a precipitate, presumably thorium *m*-nitrobenzoate, is formed, the precipitation being complete when aniline is present. Salts of lanthanum and didymium and cerous salts are not precipitated by *m*-nitrobenzoic acid, whilst ceric salts give a yellow precipitate. In order to separate thorium from these other metals, it is accordingly necessary to reduce completely, by means of hydrogen sulphide, any ceric salt present before precipitating the thorium.

A. McK.

Estimation of Vanadium. BÉARD (*Ann. Chim. anal.*, 1905, 10, 41—45).—A criticism of the various gravimetric and volumetric processes for the estimation of vanadium.

Berzelius' process (precipitation with ammonium chloride) may be rendered more accurate by adding to the mixture one-third of its volume of alcohol. A new method communicated to the author is as follows: the concentrated alkaline solution containing vanadic or hypovanadic acid is mixed with a large excess of acetic acid and precipitated with excess of nitroso- β -naphthol. The precipitate is washed with dilute acetic acid and cautiously ignited. The residue is then dissolved in ammonium carbonate, the filtrate is evaporated to dryness, and the residue calcined. It then consists of pure V_2O_5 .

L. DE K.

Estimation of Alcohol in Aqueous Solutions by the Freezing Point. RUFUS GAUNT (*Zeit. anal. Chem.*, 1905, 44, 106—108).—Below 7 per cent. of alcohol, the depression of the freezing point is proportional to the percentage of alcohol, being on the average 0.425° for

each 1 per cent. The estimation can be made with a Beckmann's apparatus in less time than is required for finding the specific gravity.

M. J. S.

Direct Estimation of Glycerol. ALEXIS A. SHUKOFF and PETER J. SCHESTAKOFF (*Zeit. angew. Chem.*, 1905, 18, 294—295).—The solution, which should contain about 1 gram of glycerol, is concentrated on a water-bath to a syrupy consistence, and then mixed with 20 grams of powdered anhydrous sodium sulphate. This absorbs all the moisture, and the glycerol may then be extracted by means of anhydrous acetone in a Soxhlet apparatus. After evaporating the acetone, the residual glycerol is dried at 75—80° to constant weight with the usual precautions.

If the sample should be alkaline, it must be slightly acidified with dilute sulphuric acid and filtered if necessary; the filtrate is then again rendered slightly alkaline with potassium carbonate. Acid samples should also be neutralised. Samples which contain more than 40 per cent. of glycerol need not be concentrated.

L. DE K.

Tribromophenol Bromide. Its Detection and Estimation. S. J. LLOYD (*J. Amer. Chem. Soc.*, 1905, 27, 7—15. See this vol., i, 277).

Tollens' Phloroglucinol and Hydrochloric Acid Reaction for Pentoses. ERW. PINOFF (*Ber.*, 1905, 38, 766—771. Compare Tollens, *Abstr.*, 1896, ii, 504).—If Tollens' reaction for pentoses is carried out in alcoholic solution and the liquid then diluted with ether, the absorption band is sharper and the colour is stable in diffused light for some weeks. If less than 1 mol. of phloroglucinol is added for each mol. of pentose, the reaction solution exhibits absorption bands in the red and blue, in addition to that in the yellow parts of the spectrum. As solutions exhibiting any one or two or all three of these absorption bands can be obtained under certain conditions, it is probable that each absorption band is due to the formation of a specific compound.

When a solution exhibiting all three bands is boiled, the band in the red, and on addition of hydrochloric acid and further boiling, the band in the blue, disappears, the absorption band in the yellow gaining in intensity.

G. Y.

Estimation of Sugar in Urine. JOSEF BILINSKI (*Monatsh.*, 1905, 26, 133—141).—A 4 per cent. solution of uranium nitrate is added to 50 c.c. of the urine to be examined until a drop of the mixture colours powdered potassium ferrocyanide brownish-red; the solution is then made up to 100 c.c. with distilled water and filtered; with a part of this solution, preliminary experiments are performed to determine the approximate amount of sugar present in the urine, and if this is found to be less than 0.6 per cent., 0.3 gram of dextrose is added. The solution is then diluted to 5—10 times its volume, and a series of portions, differing from each other by 0.1 c.c., are each heated with 6 c.c. of Fehling's solution and 2—3 drops of the uranium nitrate solution. When the amount of sugar present is equivalent to the

Fehling's solution, the upper layer of the liquid after heating is yellow, and the precipitate is yellow or red, whilst the experiment with 0.1 c.c. more of the urine solution shows a green liquid over a green or dark red precipitate. G. Y.

Detection and Estimation of Small Quantities of Maltose in the Presence of Dextrose. JULIAN L. BAKER and WILLIAM D. DICK (*Analyst*, 1905, 30, 79—83).—The authors find that Grimbert's method (Abstr., 1903, ii, 338) for removing the subsidiary products of the osazone reaction by benzene fails to give satisfactory results owing to the solubility of impure maltosazone. Cold 5 per cent. aqueous acetone removes most of the impurities without dissolving the maltosazone, but by depending on the osazone reaction alone, it is impossible to detect less than 15 per cent. of maltose in mixtures of this sugar and dextrose. Untrustworthy results are also obtained when 20 per cent. acetone is employed.

Small quantities of maltose may, however, be estimated with a fair degree of accuracy by taking the reducing power before and after inversion under standard conditions, which are given. The difference in reducing power may be due to maltose, and to confirm this the solution of the mixed sugars is fermented with *Saccharomyces Marxiannus*, which ferments the dextrose but not the maltose. A fall in the specific rotatory power and a rise in the reducing power give additional evidence of the presence of maltose. The fermented solution may also be treated with phenylhydrazine acetate in the usual way and the osazone formed identified as maltosazone by its microscopical appearance and melting point. Dextrinous substances, if present, must be removed by repeated precipitations with alcohol, or mixtures of alcohol and acetone, before the inversion and fermentation. W. P. S.

Analysis of Refined Molasses containing Reducing Sugars. HENRI PELLET (*Chem. Centr.*, 1905, i, 300; from *Bull. Assoc. Chim. Sucr. et Dist.*, 22, 373—374).—The process given by the author for the estimation of crystallisable sugar, reducing sugars, and dry residue is also suitable for the analysis of molasses from sugar refineries and for mixtures of cane-sugar and beet-sugar molasses. In all cases, the polarisation should be taken both before and after inversion. L. DE K.

Estimation of Reducing Substances in Beet-Juice. HENRI PELLET and L. PELLET (*Chem. Centr.*, 1905, i, 300—301; from *Bull. Assoc. Chim. Sucr. et Dist.*, 22, 374—378).—From 20 to 50 c.c. of the solution, which should not contain more than 3 grams of reducing sugar per litre, are mixed with an equal volume of Fehling's solution and heated in the water-bath to 87°; after heating for another 3 minutes, the liquid is diluted with half its volume of cold water, and the cuprous oxide is collected on a filter, washed with boiling water until free from alkalinity, heated in a muffle, and weighed as oxide. This, multiplied by 0.453, = reducing sugars. Large amounts of cupric oxide are better estimated by titration with stannous chloride

instead of by weighing. If possible, the use of lead acetate in order to clarify the solution should be avoided. If much calcium is present in the liquid, this may be removed by the judicious addition of sodium carbonate.

L. DE K.

Determination of the Decomposition-Velocity of Nitro-cellulose. PAUL OBERMÜLLER (*Chem. Centr.*, 1905, i, 472—473; from *Mitt. Berl. Bezirksver. Verein Deutscher Chemiker*, 11/10, 1904).—About 2 grams of the sample, from which the greater portion of the moisture has been removed by pressure, are heated in a small weighed tube placed in a calcium chloride bath, heated at 140°, and connected with a mercury manometer and a special vacuum apparatus. After about 10 minutes, when the remaining water has evaporated, the connection with the pump is broken off and every 15 minutes the pressure is recorded of the gases given off owing to decomposition. Finally, the tube is reweighed and the results are calculated on one gram of the heated substance.

A specimen of good gun-cotton caused a pressure of 19, 41, 66, and 95 mm. in 15, 30, 45, and 60 minutes respectively. In the case of a sample of collodion wool, the pressures amounted to 15, 31, 51, and 75 mm. respectively.

L. DE K.

Source of Error in the Estimation of Acetone by the Iodoform Process. WILHELM VAUBEL and O. SCHEUER (*Zeit. angew. Chem.*, 1905, 18, 214—215).—Messinger estimates the amount of acetone by adding potassium hydroxide and then an excess of standard iodine solution, which causes its conversion into iodoform. The excess of iodine is then titrated by acidifying with dilute sulphuric acid and titration with thiosulphate.

The authors state that the process gives satisfactory results provided the iodine is not titrated with thiosulphate, but with standard arsenious acid in the presence of an alkali hydrogen carbonate.

L. DE K.

Formic Acid and its Volumetric Estimation. ERWIN RUPP (*Arch. Pharm.*, 1905, 243, 69—73).—The officinal formic acid of the German pharmacopœia can be prepared from the commercial acid, which is now manufactured in a state of considerable purity by the action of carbon monoxide under pressure on powdered sodium hydroxide, &c. This is allowed to remain for a day with a little litharge (1 gram per litre), being shaken frequently; it is then distilled: this is to remove hydrochloric acid. The distillate is diluted to the sp. gr. 1.063, allowed to remain 1 to 1½ days, and then filtered from the slight deposit (of sulphur?).

For the volumetric estimation, a hypobromite solution is prepared by dissolving 15 grams of sodium hydroxide (pure by alcohol) in about 450 c.c. of water in a 500 c.c. flask, allowing to cool, adding 5 c.c. of bromine, shaking until this has dissolved, and diluting to the mark. This solution is standardised by diluting 5 c.c. in a stoppered bottle with 50—75 c.c. of water, adding 20 c.c. of 10 per cent. hydrochloric acid, and, immediately after this, 1 gram of iodine; after 1—2 minutes,

the iodine liberated is titrated with *N*/10 thiosulphate. The hypobromite solution keeps well in a closely-stoppered bottle in the dark ; after three months, no appreciable change in strength occurred. For the actual estimation, a suitable volume of this solution is diluted in a stoppered bottle to 70—100 c.c. ; a measured quantity of the formic acid is added, sufficient to reduce about half of the hypobromite ; dilute hydrochloric acid is added drop by drop until the yellow colour of bromine is just permanent where the drop falls in, and the whole is allowed to remain half an hour in the dark. Then 1 gram of potassium iodide and 10—20 c.c. of dilute hydrochloric acid are added, and the iodine liberated is titrated with *N*/10 thiosulphate. The difference between the volume of thiosulphate solution now used and that equivalent to the amount of hypobromite solution taken measures the amount of formic acid ; 1 c.c. = 0.0023 gram $\text{H}\cdot\text{CO}_2\text{H}$. Error - 0.2 to + 0.2 per cent. of the whole, when 11 c.c. is the measure of the formic acid.

C. F. B.

Detection of Foreign Oils in Nut Oil. J. BELLIER (*Ann. Chim. anal.*, 1905, 10, 52—59).—Into two test-tubes are introduced respectively 1 c.c. of pure nut oil and 1 c.c. of the suspected sample. Five c.c. of alcoholic potassium hydroxide (16 grams in 100 c.c.) are added, and the tubes are heated nearly to boiling until the fat has dissolved. After closing the tubes, they are placed for half an hour in water at 70° and then mixed with a previously ascertained quantity of acid (1 vol. glacial acetic acid, 3 vols. of water) sufficient to neutralise the alkali. The tubes are then again corked and placed in water at 17—19° and shaken frequently.

Pure nut oil hardly gives a precipitate, but poppy-seed oil, if not present in too small amount, causes an abundant deposit. Other oils, such as olive, sesamé, cotton, pea-nut, linseed, colza, and rape seed, often cause such a deposit that the whole mass appears solid.

L. DE K.

Detection of Saccharin in Wine. ED. MACKAY CHACE (*J. Amer. Chem. Soc.*, 1904, 26, 1627—1630).—Fifty c.c. of the wine are extracted in the usual manner with ether and with light petroleum of low boiling point, and the extracted matter, after evaporation of the ether, is again extracted with light petroleum. This extract is returned to the dish containing the residue from the extraction with light petroleum, and, after diluting to 10 c.c., 1 c.c. of dilute sulphuric acid (1 : 2) is added and the mixture heated to boiling. If salicylic acid should be present, an excess of a 5 per cent. solution of potassium permanganate is added and the boiling continued for one minute, but in the absence of this acid there is no need for further boiling. A small piece of sodium hydroxide is now added, the filtrate is evaporated to dryness in a silver dish, and the residue heated for 20 minutes at 210—215°. This converts any saccharin into salicylic acid, which is then tested for as usual.

L. DE K.

General and Physical Chemistry.

Refractive Indices of the Elements. CLIVE CUTHBERTSON (*Phil. Trans.*, 1905, A. 204, 323—349).—Details are given of work already described (this vol., ii, 129). J. C. P.

Ultra-violet Absorption of Organic Dyes. PAUL KRÜSS (*Zeit. physikal. Chem.*, 1905, 51, 257—296).—The main classes of substances investigated by the author are the azo-compounds, the derivatives of triphenylmethane, and the components of the azo-dyes. Details are given of the absorption spectra, and the paper is illustrated by a number of plates. The solvents used were water and ethyl alcohol; in some cases, strong sulphuric acid also was employed. The colourless bases and components of the dyes are all characterised by marked ultra-violet absorption bands. The intensity and breadth of the absorption bands of the various dyes are, in general, less in the ultra-violet than in the visible part of the spectrum. The ultra-violet absorption of one group of dyes is characteristically different from that of another group; within a given group, the general character of the absorption remains the same, constitutional differences being revealed by a greater or smaller displacement of the absorption bands. It is thus possible in many cases to settle the group to which a dye belongs by examining a photograph of its absorption spectrum. In the case of the azo-dyes, introduction of methyl groups in the aniline part of the molecule has but slight influence on the position of the absorption bands; substitution, however, in the naphthalene part of the molecule has a much greater effect on the character of the ultra-violet absorption, and the magnitude of the effect depends on the position of the substituent group. It is not permissible to study the absorption of azo-dyes in concentrated sulphuric acid solution, for the latter exerts more than a merely solvent action except when the dyes are already sulphonated. The author's work confirms the view that ultra-violet absorption increases with the number of double bonds in the molecule. The fastness to light of the dyes is no doubt intimately connected with the ultra-violet absorption, but to deduce the relative fastness from the amount of absorption is permissible only with dyes of similar constitution; it is not always the dye showing the strongest ultra-violet absorption which bleaches most rapidly in sunlight, as may be shown especially in the case of the azo-dyes.

The paper contains a review of the work previously done on the absorption spectra of organic dyes. J. C. P.

Phosphorescence caused by the Beta and Gamma Rays of Radium. Parts I and II. GEORGE T. BEILBY (*Proc. Roy. Soc.*, 1905, 74, 506—510, 511—518).—When canary-yellow crystals of barium platinocyanide are placed on the mica cover of a cell containing radium bromide, the colour changes from yellow to red, and the phosphorescence falls rapidly to about 1/12th of its original value; further, the phos-

phorescence of the reddened crystals ceases immediately on their removal from the action of the rays. The original yellow colour and phosphorescent value are restored completely by recrystallisation of the red crystals; the restoration is not effected by exposure to sunlight, as stated by some observers. It is shown that the reduction of the phosphorescent value accompanying the change from yellow to red is not due to chemical decomposition or to loss of water of crystallisation, and the author propounds the view that it is associated with a change from the crystalline to the amorphous condition (compare Abstr., 1904, ii, 647), a view supported by his experiments. Thus the colour change and the reduction of phosphorescent value may be brought about simply by bruising and flowing the yellow crystals on a glass plate. The amorphous product obtained in this way and the reddened crystals obtained by the action of the β -rays are both reconverted on heating into the yellow state, and the phosphorescent value is raised in both cases.

Very often, as with barium platinocyanide, phosphorescent phenomena may be attributed to physical changes. The molecular movement required to bring about these changes may be produced by heat, by mechanically applied stress, or by radiant energy. Other types of phosphorescence are distinguished by their appearance in three stages: primary, secondary, and revived phosphorescence: primary phosphorescence is the luminescence produced under the direct influence of a stimulus; secondary phosphorescence is the luminescence which continues after the direct stimulation has ceased; revived phosphorescence is the luminescence revived by heat after the secondary phosphorescence has diminished or ceased altogether. In cases where secondary or revived phosphorescence is observed, the effects must be referred to the play of chemical affinity. The author has studied the action of the β - and γ -rays on rock crystal, calcspar, potash glass, flint glass, potassium iodide, bromide, and chloride, specially in reference to the colour changes produced, and the secondary and revived phosphorescence. The observed phenomena support the view that when solids are exposed to the β - or cathode-rays a sort of electrolysis takes place, that the products of electrolytic dissociation are insulated or partly insulated from each other by the neutral molecules, as in a viscous electrolyte, and that it is the breaking down of this insulation and the recombination of the ions which causes revived phosphorescence. Additional experiments at -100° confirm the view that a low temperature increases the insulating power of the molecules, enabling some substances (for example, barium platinocyanide) to store chemical energy which are unable to do so at all at higher temperatures, and increasing the storage capacity of others (for example, potassium chloride and bromide).

J. C. P.

Theory of Photographic Processes. Chemical Dynamics of Development. S. E. SHEPARD and C. E. KENNETH MEES (*Proc. Roy. Soc.*, 1905, 74, 447—473).—The authors' results are summarised as follows: if T is the optical transparency of the silver deposited in photographic processes, then the density D (which = $-\log T$) is accurately proportional to the mass of silver. From considerations of the growth

of the density during development and of the theory of heterogeneous reactions, the equation $1/t \cdot \log D_{\infty} / (D_{\infty} - D) = K$ is deduced, and the experimental results are in harmony with this formula. The velocity of development, as measured by the constant K , is directly proportional to the concentration of the reducer, is affected by the age and condition of the plate, and is reduced by the addition of soluble bromides, not, however, in the proportion which would occur if the velocity of the chemical reaction $\text{Ag} + \bar{\text{R}} = \text{Ag}(\text{met.}) + \bar{\text{R}}$ alone were measured. It thus appears that the velocity of development depends mainly on the rate of diffusion to the affected haloid. The law of constant density-ratios due to varying exposures, deduced from the above theory, is experimentally confirmed. The development-factor γ in the sensitometry equation $D = \gamma(\log E/i)$ is governed by the same laws as a single density. Methods for calculating and controlling γ are given, by means of the equation $1/t \cdot \log \gamma_{\infty} / (\gamma_{\infty} - \gamma) = K$. By means of this expression, the velocities with ferrous oxalate, fluoride, and citrate were compared, the relative values of K being in $N/10$ concentration 0.0487, 0.003, and 0.001.

J. C. P.

Photographic Activity of Ozone. KARL SCHAUM (*Chem. Centr.*, 1905, i, 580; from *Physikal. Zeit.*, 6, 73—74).—The variable sensitiveness of gelatin plates to ozonised oxygen, when hydrogen peroxide is absent, is due to differences in the quality of the gelatin.

G. D. L.

Spontaneous Action of Metals on Sensitive Films of Photographic Plates without Direct Contact. GEORG W. A. KAHLBAUM and MAX STEFFENS (*Chem. Centr.*, 1905, i, 579; from *Physikal. Zeit.*, 6, 53—60).—Metallic plates, whether submitted or not to radium or X-rays, act on photographic plates. Zinc and aluminium plates, acting on a plate placed above them, lose this power after exposure to X-rays, but act on a plate placed below as before; moisture and heat modify the intensity of the action. Actinograph appears to result from heavy emanations. Zinc and seemingly aluminium and the radioactive uranium give images on plates placed both above and below, the other metals giving images only on those placed below them.

G. D. L.

Origin of Radium. BERTRAM B. BOLTWOOD (*Phil. Mag.*, 1905, [vi], 9, 599—613. Compare *Abstr.*, 1904, ii, 666).—The general method of investigation previously employed (*loc. cit.*) has been extended to twenty-two different samples, comprising twelve distinct mineral species. It is found, in harmony with the earlier work, that the quantities of uranium and radium occurring together are directly proportional. The only possible conclusion is that uranium is the parent of radium. The participation of thorium in the production of radium is excluded by the fact that the radium-uranium ratio is independent of the percentage of thorium in the minerals. It is highly probable, as suggested by Rutherford, that intermediate stages exist between the uranium atom and the

radium atom. The persistent appearance of lead as a constituent of uranium-radium minerals may indicate that this element is one of the final disintegration products of uranium. The only mineral examined by the author which was found practically free from lead was a sample of uranophane from North Carolina. This is geologically the youngest of the minerals examined, and it would naturally contain very little lead if this element was a final disintegration product.

The author's experiments show that monazite from various sources contains 0.3—0.4 per cent. of uranium. The presence of notable quantities of uranium and radium in monazite explains the accumulation of helium in this mineral, for monazite is geologically very old, and the production of helium through radium from uranium has doubtless been going on for countless ages. J. C. P.

Radiation from Hydrogen Peroxide. J. PRECHT and C. ORSUKI (*Chem. Centr.*, 1905, i, 653; from *Ber. Deut. phys. Ges.*, 3, 53—56).—The permeability of various substances for the radiations from hydrogen peroxide was tested photographically and chemically by means of gelatin plates containing titanium dioxide in sulphuric acid. Gelatin, celluloid, paper, and Canada balsam are penetrated, paraffin, ebonite, glass, and metals (including aluminium) are not.

A strong current of air does not prevent some hydrogen peroxide from reaching the plate, and the effect of varying the concentration of the peroxide is in accordance with the law of vaporisation of binary liquid mixtures. The phenomena are due to volatilisation of the peroxide, and not to radiation as supposed by Graetz (*Physikal. Zeit.*, 5, 698). G. D. L.

Radiation from Ordinary Materials. NORMAN R. CAMPBELL (*Phil. Mag.*, 1905, [vi], 9, 531—544).—The author has measured the spontaneous saturation current (or "leak") through vessels of various forms and materials. It appears that the influence which the walls of a containing vessel exert on the spontaneous ionisation of the enclosed air is due to a radiation proceeding from the walls. Part of this radiation from certain materials, such as tin, zinc, graphite, and platinum, is analogous to the secondary radiation excited by Röntgen and other rays. The absorption-coefficient of air for the radiation is comparable with that of air for the α -radium rays, and is different for different materials. Hence the radiation is not likely to be due to radioactive impurities, but is probably an inherent property of the material. There is no evidence of rays from ordinary materials of a penetrating power considerably greater than that of the α -rays from radioactive elements. J. C. P.

Radioactivity and Chemical Change. NORMAN R. CAMPBELL (*Phil. Mag.*, 1905, [vi], 9, 545—549).—When a chemical reaction takes place in contact with the outside of a vessel, there is, in general, a change in the spontaneous leak within the vessel. This has been regarded by some investigators as evidence that chemical change is accompanied by radioactivity, but the author shows that the phenomenon is due to the heating of the walls of the vessel. Chemical

actions which develop heat sometimes cause an increase and sometimes a decrease in the leak, but the sign of the change is the same as that of the change due to heat. Chemical reactions which are accompanied by the evolution of gases cause an increase in the leak, but this increase is more readily explained by the ionisation of the gases than by a process of ray-emission. J. C. P.

Heat Actions of Radium Bromide, Naphthalene, and Camphor. N. A. HESSEHUS (*J. Russ. Phys. Chem. Soc.*, 1905, 37, ii, 1—9).—The actions of naphthalene and camphor on both ordinary and electric thermometers are similar to that of radium, but only about one-third as strong. These observations confirm the conclusion already drawn from previous experiments made by the author and by Georgiewsky (*J. Russ. Phys. Chem. Soc.*, 1903), namely, that the rise of temperature indicated is due mainly to the absorption of the radium emanations by the thermometers themselves. T. H. P.

Ionisation produced between Parallel Plates by Radium Emanation. WILLIAM DUANE (*Compt. rend.*, 1905, 140, 786—788).—Air containing radium emanation was introduced into a chamber containing two parallel plates and the ionisation current between the plates for a considerable difference of potential was determined: (1) immediately after the introduction of the emanation, (2) three hours later, and (3) half an hour after the emanation had been removed by a current of air. In the first case, the observed current is due to the emanation, in the second, to the sum of the effects of the emanation and of the imparted activity, and in the third case to the third substance *C* of the imparted activity. Formulæ are given showing the dependence of the current on the distance between the electrode plates in each of the three cases.

Assuming that the charge on an ion is 3×10^{-10} electrostatic units, the maximum number of ions of each sign produced by unit quantity of the emanation per second is 2.1×10^9 . It is also calculated that the energy involved in the production of the emanation from radium bromide corresponds with about one-twentieth of the total heat disengaged by the radium salt, and further that 14,500 ions of each sign are produced in the destruction of a molecule of emanation.

H. M. D.

Photoelectric Phenomena exhibited by Moist Silver Iodide. HERMANN SCHOLL (*Ann. Physik*, 1905, [iv], 16, 193—237, 417—463).—Silver iodide which is immersed in aqueous salt solutions and exposed to light undergoes, especially in presence of free iodine, a process of dissociation which produces the ions of silver iodide and probably also negative electrons. The latter are much more mobile in the solid silver iodide than electrolytic ions, and impart metallic conductivity to the silver iodide. The dissociation process referred to is induced by light of all wave-lengths, but the extent to which it takes place runs parallel with the absorptive power of the silver iodide. The author's experiments indicate also that the action of light results in the production of a new substance from silver iodide, the production,

however, being unaccompanied by the liberation or absorption of free iodine. This substance also is photoelectrically sensitive, is unstable, and is therefore formed only up to a certain equilibrium concentration, which depends on the intensity and colour of the illumination.

J. C. P.

Electrical Conductivity and other Properties of Sodium Hydroxide in Aqueous Solution as elucidating the Mechanism of Conduction. WILLIAM R. BOUSFIELD and THOMAS M. LOWRY (*Phil. Trans.*, 1905, A, 204, 253—322).—A full account of work that has been described previously (this vol., ii, 135).

J. C. P.

Electrical Conductivity of Liquid Ammonia Solutions. II. EDWARD C. FRANKLIN and CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1905, 27, 191—222. Compare Abstr., 1900, ii, 382).—In continuation of the work on this subject, the investigation has been extended to the following substances: formamide, chloroacetamide, cyanoacetamide, phenylacetamide, benzamide, thiobenzamide, phthalimide, cyanamide, sulphamide, nitroamide, methylnitroamine, nitroguanidine, urethane, ammonium nitrourethane, mercury succinimide, sodium nitromethane, tetranitromethane, trinitrobenzene, trinitroaniline, aurous cyanide and the cyanides of potassium, mercury, silver, and zinc, nitrates of lithium, sodium, potassium, thallium, silver, and barium, chlorides of sodium and ammonium, bromides of sodium and ammonium, iodides of sodium, ammonium, and silver, hydrochlorides of ethylamine and diethylamine, and water.

The results of the experiments are tabulated and are also plotted as curves. The specific conductivity of liquid ammonia at its boiling point is below 0.01×10^{-6} Kohlrausch units. The amides are, in most cases, readily soluble in liquid ammonia, and whilst those of the weaker acids have a low conductivity, those of the stronger acids are good conductors; thus a solution of carbamide is scarcely capable of conducting the current at all, that of formamide conducts much better, and those of the amides of the strong sulphonic acids and of nitric and sulphuric acids are excellent conductors. As stated in the previous paper, the nitro-compounds of both aliphatic and aromatic hydrocarbons are generally readily soluble in liquid ammonia, forming solutions which conduct well. Nitromethane unites with ammonia at -33° to form two crystalline additive compounds, $\text{CH}_3 \cdot \text{NO}_2 \cdot 2\text{NH}_3$ and $\text{CH}_3 \cdot \text{NO}_2 \cdot \text{NH}_3$, both of which lose their ammonia at the ordinary temperature and pressure. Tetranitromethane yields an additive compound, $\text{C}(\text{NO}_2)_4 \cdot \text{NH}_3$, but is decomposed by excess of ammonia with formation of ammonium trinitromethane, $\text{CH}(\text{NO}_2)_3 \cdot \text{NH}_3$, which dissolves very easily in liquid ammonia to form a solution of good conductivity. The stronger solutions of cyanoacetamide and the cyanides of the heavy metals in liquid ammonia exhibit a decrease of molecular conductivity with increasing dilution; as the dilution is further increased, the conductivity passes through a minimum and then gradually rises. The salts of univalent metals with univalent acid radicles show a great variation in conductivity and degree of

ionisation with the dilution. The behaviour of solutions of these salts in liquid ammonia is compared with the behaviour of their aqueous solutions. E. G.

Anodic Decomposition during the Electrolysis of Certain Thallium, Bismuth, and Silver Salts. MARGRETE BOSE (*Zeit. anorg. Chem.*, 1905, 44, 237—266).—The products of decomposition at the anode during the electrolysis of aqueous solutions of certain thallium, bismuth, and silver salts have been investigated. The electrolysis was conducted in each case at the ordinary temperature, and with electrodes which were not attacked.

The anodic decomposition curves for thallium nitrate exhibit two decomposition points, of which the higher, corresponding with 1.428 volts, indicates the formation of the oxide Tl_2O_3 , whilst the lower, corresponding with 1.08 volts, also indicates the formation of another oxide, which was formed in small amount only. The curves for thallium sulphate exhibit the higher decomposition point only, thus indicating the formation of the oxide Tl_2O_3 . A characteristic, momentary separation of hydroxide was observed in the liquid whenever a definite tension had been exceeded. The anodic curves for bismuth nitrate solutions exhibit a decomposition point corresponding with 1.86 volts, whilst a bright yellow oxide, probably Bi_2O_3 , is produced. At higher tensions, ozonised oxygen is evolved in considerable amount from the surface of the bismuth oxide. The curves for silver nitrate and for silver sulphate show a very sharp decomposition point, corresponding with 1.573 and 1.53 volts respectively. The difference between the positions of these two points is interpreted as with the thallium salts. The oxide precipitated in each case is identical, and is probably Ag_2O_2 . The interpretation of other authors, that the products which are separated at the anode from solutions of silver nitrate and of silver sulphate are compounds of one or several silver oxides with the corresponding acids, is not correct. The assumption of such compounds is not necessary if the analytical difficulties are considered, and especially since compounds which are electrolytically separated readily retain mechanically small amounts of the liquid from which they are deposited.

The thallium oxide and bismuth oxide which separate appear to be non-conductors, while the silver oxide is a conductor. A. McK.

Electrostenolysis and Faraday's Law. THEODORE W. RICHARDS and BURRITT S. LACY (*J. Amer. Chem. Soc.*, 1905, 27, 232—233. Compare Richards and Stull, *Abstr.*, 1903, ii, 259).—Electrostenolysis, or the deposition of certain metals in capillary tubes during the passage of a current, was first observed by Braun, and an explanation of the phenomenon has been put forward by Coehn (*Abstr.*, 1898, ii, 365).

Experiments are described, the results of which are in accord with Coehn's hypothesis, and prove that the complication of electrostenolytic deposition does not affect the weight of the true cathode deposit or the exact application of Faraday's law. E. G.

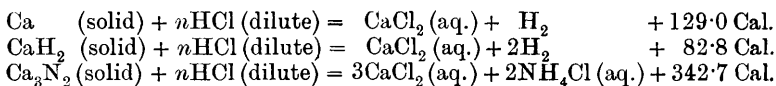
Modifications of the Thermometer used in the Determination of Molecular Weights and for the Measurement of Small Differences of Temperature. ERNST BECKMANN (*Zeit. physikal. Chem.*, 1905, **51**, 329—343).—A description of the various modifications, chiefly of the reservoir, that have been tried in the course of evolution of the Beckmann thermometer. The paper is profusely illustrated. J. C. P.

Atomic Heat of Solid Elements. RUDOLF LAEMMEL (*Ann. Physik*, 1905, [iv], **16**, 551—557).—In depreciating Dulong and Petit's "Law," the author emphasises the variation with temperature of the specific heats of the solid elements. It is suggested, however, that the elements are comparable at their melting points, and it is shown that the atomic heats calculated for these temperatures lie between 9 and 10 calories for a number of elements; there are on the other hand a good many exceptions.

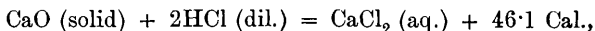
The specific heats of aluminium, chromium, manganese, and lithium have been determined for various temperatures by the author and other workers in the same laboratory. The formulæ expressing the variation of specific heat (s) with temperature (t) are as follows: aluminium, $s = 0.208897 + 1.61868t.10^{-4} - 2.94246t^2.10^{-7} + 4.6183t^3.10^{-10}$; chromium, $s = 0.103944 + 1.0591t.10^{-4} - 2.9694t^2.10^{-7} + 5.4088t^3.10^{-10}$; manganese, $s = 0.10722 + 7.8012t.10^{-5} - 1.1085t^2.10^{-7} + 3.8178t^3.10^{-10}$; lithium, $s = 0.7951 + 2.0632t.10^{-3} + 2.5083t^2.10^{-6} + 1.4207t^3.10^{-8}$.

J. C. P.

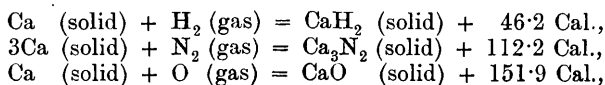
Heat of Formation of the Hydride and Nitride of Calcium. ANTOINE GUNTZ and HENRY BASSET, jun. (*Compt. rend.*, 1905, **140**, 863—864).—Electrolytic calcium was purified by distilling in a vacuum, the metal being condensed in a tube of polished iron cooled by a current of water. In these circumstances, the metal was readily obtained in crystalline fragments. The hydride and nitride were prepared by heating in a current of hydrogen or nitrogen, and the following heats of solution were determined:



On the basis of Berthelot's determination,



the heats of formation,

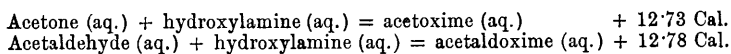


are calculated.

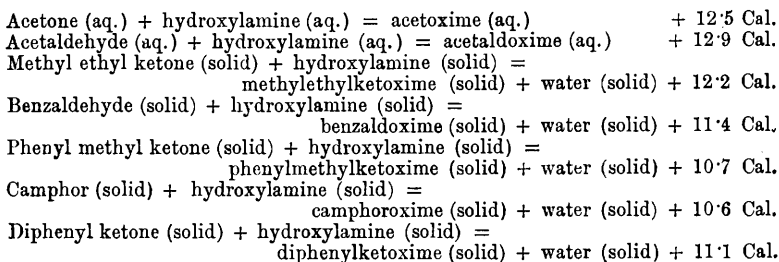
The value given by Thomsen for the heat of formation of calcium oxide is 131.5 Cal. This is 20.4 Cal. smaller than the value calculated by

the authors. Since the heats of formation of the calcium compounds all rest upon this value given by Thomsen, it follows that these heats of formation are very far from being correct. Instead of the heat of formation of calcium carbide being -7.25 Cal., the correct value according to the authors' measurements is $+13.15$ Cal. H. M. D.

Heat of Formation of the Oximes. PH. LANDRIEU (*Compt. rend.*, 1905, 140, 867—870).—The heats of formation of acetoxime and acetaldoxime were determined in the first instance by experiments carried out in aqueous solution, the reaction taking place with sufficient rapidity in alkaline solution :

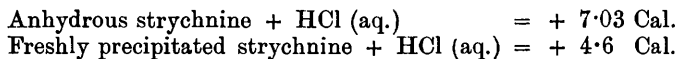


A larger number of data were obtained by measurement of the heats of combustion of the crystalline oximes in the calorimetric bomb, these in some cases being combined with measurements of the heats of solution. The following numbers were obtained in this way :

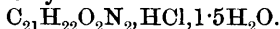


H. M. D.

Thermochemical Investigation of Strychnine and Brucine. MARCELLIN BERTHÉLOT and GAUDECHON (*Compt. rend.*, 1905, 140, 753—761).—*Strychnine*.—Heat of formation from the elements $+53.6$ Cal. Freshly precipitated strychnine is hydrated and in its transformation into anhydrous strychnine 3—3.5 Cal. are developed.



Crystalline strychnine hydrochloride has the composition



It readily loses water at 120° . When dissolved in 75 parts of water, the hydrated salt absorbs -5.8 Cal., whilst the anhydrous salt absorbs -1.2 Cal. The heat of formation of the anhydrous salt is $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$ (anhydrous) $+ \text{HCl (gas)} = \text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2, \text{HCl (solid)} + 25.6$ Cal. Normal strychnine sulphate, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_2, \text{H}_2\text{SO}_4$, forms a hexahydrate and a dihydrate. The acid sulphate, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2, \text{H}_2\text{SO}_4$, is obtained anhydrous, or as a dihydrate. The heats of dissolution in about 120 parts of water are -6.42 , $+3.12$, and 5.33 Cal. respectively. The heat of formation of the acid sulphate is $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2$ (anhydrous) $+ \text{H}_2\text{SO}_4$

(cryst.) = $C_{21}H_{22}O_2N_2 \cdot H_2SO_4$ (anhydrous) + 23.05 Cal. Crystallised strychnine acetate, $C_{21}H_{22}O_2N_2 \cdot C_2H_4O_2 \cdot 1.5H_2O$, does not dissolve completely in water unless excess of acetic acid is present. The heat of solution of the crystalline salt in 120 parts of water is +3.9 Cal., the heat of solution of precipitated strychnine in dilute acetic acid being +3.5 Cal.

Brucine.—Carefully purified and fractionally precipitated brucine gave numbers on analysis corresponding with the formula $C_{23}H_{26}O_4N_2$. On bringing the anhydrous substance into contact with water, an appreciable amount of heat is developed. Brucine precipitated by ammonia from solutions of its salts contains $4H_2O$; 2 mols. are lost on exposure to air at the ordinary temperature, and the remainder is given off at 110° or over sulphuric acid. Brucine is monobasic, but only dissolves in water completely when excess of acid is present. Heat of solution in dilute hydrochloric acid: Anhydrous brucine + 11.2 Cal., Brucine, $2H_2O$ + 6.8 Cal., Brucine, $4H_2O$ = +4.36 Cal.

From an aqueous alcoholic solution of brucine, crystals of the composition $C_{23}H_{26}O_4N_2 \cdot C_2H_6O \cdot 2H_2O$ are obtained. The heat of solution of this compound in dilute hydrochloric acid is +5.42 Cal. Crystalline brucine hydrochloride, $C_{23}H_{26}O_4N_2 \cdot HCl \cdot 4H_2O$, loses $3H_2O$ on exposure to the air at the ordinary temperature. On heating at 130° , the anhydrous salt is obtained. The heats of dissolution in dilute hydrochloric acid are for the tetrahydrate -6.96 Cal., for the anhydrous salt +4.36 Cal. Heat of formation of brucine hydrochloride: Brucine (solid) + HCl (gas) = Brucine, HCl (anhydrous) + 23.9 Cal.

Anhydrous brucine hydrochloride absorbs more than four molecules of hydrogen chloride. The quantities of heat developed in the combination of the first, second, third, and fourth molecules are respectively +23.5, 14.5, 10.5, and 10.4 Cal.

Crystalline brucine sulphate, $C_{24}H_{26}O_4N_2 \cdot H_2SO_4 \cdot 6.5H_2O$, dissolves in dilute sulphuric acid with absorption of -7.26 Cal. H. M. D.

Thermal Study of the Acid Function of Pyruvic Acid. Influence of Ketonic Oxygen. GUSTAVE MASSOL (*Bull. Soc. chim.*, 1905, [iii], 33, 335—337).—The solution of a gram-mol. of liquid pyruvic acid in 2 litres of water develops 4.28 Cal. The solid, crystalline polymeride, obtained by exposure of syrupy pyruvic acid under reduced pressure over sulphuric acid and subsequent stirring with a platinum rod, melts at 92° (pyruvic acid solidified by refrigeration melts at 13.6°), has the mol. weight 275 (determined cryoscopically in acetic acid solution, in which it is slowly depolymerised), and on solution of a gram. mol. in 2 litres of water absorbs 0.08 Cal., whence the molecular latent heat of fusion = 4.36 Cal., neglecting the small heat of condensation.

When 1 mol. of sodium hydroxide is added to a gram-mol. solution of pyruvic acid in 2 litres of water, 11.80 Cal., and, on the addition of a second gram-mol. of the hydroxide, 1.87 Cal., are developed. The heat of solution of sodium pyruvate is 2.56 Cal., whence the heat of formation of the solid sodium salt from the solid acid is 25.6 Cal. and from the liquid acid 21.24 Cal.

The heat of neutralisation of pyruvic acid is smaller than that of

acetic or propionic acid, whilst the heats of formation of the solid sodium salts of the latter are larger than that of sodium pyruvate.

T. A. H.

Determination of Some Heats of Mixture. B. MAY CLARKE (*Chem. Centr.*, 1905, i, 916; from *Physikal. Zeit.*, 6, 154—159).—The heats of mixture of alcohol and water, aniline and xylene, propyl alcohol and water, chloroform and water, xylene and amyl alcohol, chloroform and xylene, and of alcohol and amyl ether have been determined by means of a Bunsen ice calorimeter protected by a Dewar vessel, cotton-wool packing, and a thick layer of ice. In the cases of mixtures of water and alcohol, aniline and xylene, and propyl alcohol and water, the heat toning was found to vary with the change of volume, the maxima on the corresponding curves lying practically at identical positions. This coincidence appears, however, to be accidental, for in other cases, as, for example, that of chloroform and ether, a large heat toning may correspond with a small change of volume.

E. W. W.

Cryoscopic Measurements with Hydrogen Cyanide. ROBERT LESPIEAU (*Compt. rend.*, 1905, 140, 855—857).—The lowering of the freezing point of liquid hydrogen cyanide on addition of ethyl alcohol, chloroform, benzene, water, trichloroacetic acid, and sulphuric acid has been measured. The molecular lowering decreases somewhat as the concentration increases, and this decrease is very considerable when the dissolved substance is water or benzene. Extrapolated to zero concentration of the dissolved substance, the value of the molecular lowering is almost the same (19—20) for each of the substances enumerated. In the case of potassium iodide and potassium nitrate, the molecular lowering is almost twice as large (39—40). The observations are compared with the electrical conductivity measurements of Kahlenberg for hydrogen cyanide solutions. Solutions of trichloroacetic acid and sulphuric acid in this solvent are feeble conductors, whereas potassium salts are good conductors, and the author considers that these facts are in accord with the cryoscopic measurements.

H. M. D.

Joule-Thomson Effect in Carbon Dioxide. F. E. KESTER (*Chem. Centr.*, 1905, i, 596; from *Physikal. Zeit.*, 6, 44—50).—The results obtained by allowing the gas to pass under pressure through a plug of cotton-wool in an ebonite cylinder are expressible at 22° by the equation $d\theta/dp = 1.187^\circ + 0.0015 p$. The variation of $d\theta/dp$ with p is greater than would follow from Van der Waals' equation.

G. D. L.

Apparatus for determining the Specific Gravity of Solid Fats and Waxes. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 83—85).—This apparatus consists of a light, graduated, stoppered test-tube fitted on a foot and containing from 7 to 15 c.c. From 5 to 10 c.c. of 70 to 90 per cent. alcohol is carefully run into the tube from a pipette or burette, the volume of the liquid accurately

determined, and the whole apparatus weighed. From 1.5 to 2 c.c. of the fat or wax are added in small pieces and the increase of weight and volume measured. The specific gravity of the fat or wax can then be readily calculated. Water may be used in place of alcohol for substances heavier than, and insoluble in, water.

With this apparatus, the specific gravity of cocoanut oil is found to be 0.9702 at 20°. T. H. P.

Application of Watt's Principle to the Dissociation of the Carbonates of Lead and Silver. ALBERT COLSON (*Compt. rend.*, 1905, 140, 865—867).—According to Debray's experiments, the reaction $\text{PbCO}_3 = \text{PbO} + \text{CO}_2$ is not a reversible change. According to the author, white oxide of lead absorbs carbon dioxide readily, but the oxide which results from the decomposition of lead carbonate at 350° has not this property; it has, moreover, a yellow colour and is probably polymerised. When a small quantity of water vapour is introduced into the dissociation apparatus containing the yellow oxide in contact with an atmosphere of carbon dioxide at 180°, the gas is slowly absorbed, especially if the surface of the oxide exposed to the gas is renewed. It is concluded that the decomposition of lead carbonate becomes reversible if the disturbances due to polymerisation of the oxide are eliminated; this appears to be possible in the presence of water vapour. Water vapour is also found to greatly accelerate the establishment of the equilibrium which is ultimately set up when lead carbonate is heated at different temperatures. In a moist atmosphere, the equilibrium condition is reached in 6—7 hours, whereas if the lead carbonate is completely dried by means of phosphoric oxide, this time interval is increased ten to twelve times. The values obtained for the tension of dissociation of lead carbonate (1) in a perfectly dry atmosphere, (2) in an atmosphere saturated with water vapour at a pressure corresponding with 0°, the pressure of the water vapour being corrected for, are as follows:

Temperature:	184°.	210°.	233°.	280°.
(1)	10	32.5	102	548
(2)	12	33	104	

H. M. D.

Thickness and Tension of the Capillary Layer. GERBIT BAKKER (*Zeit. physikal. Chem.*, 1905, 51, 344—367. Compare Abstr., 1904, ii, 540).—A mathematical treatment of the relationships existing between the thickness of the capillary layer, the capillary constant, the densities of liquid and of vapour, and the temperature. From the available experimental data, the author concludes that the thickness of the capillary layer for soap solutions at the ordinary temperature lies between 5 $\mu\mu$ and 25 $\mu\mu$. J. C. P.

Distribution of Soluble Substances between Water and Aromatic Hydrocarbons. WALTER HERZ and HERBERT FISCHER (*Ber.*, 1905, 38, 1138—1144. Compare this vol., ii, 79).—Measurements are given of the distribution between water and benzene,

toluene, and the three xylenes, of acetic, chloroacetic, and picric acids, trimethylamine, acetone, and phenol. As acetic and chloroacetic acids form double molecules when dissolved in aromatic hydrocarbons, a constant value was found for the ratio: $\sqrt{\text{concentration in hydrocarbon} / \text{concentration in water}}$. This ratio gives a constant value only for concentrated solutions, as the acids tend to become unimolecular in dilute solutions. With picric acid, when allowance has been made for its degree of dissociation in water, the above ratio approaches a constant value with increasing concentration. With phenol, which at first is bimolecular, the constant value above a certain concentration is for the ratio: $\sqrt[3]{\text{concentration in hydrocarbon} / \text{concentration in water}}$; in highly concentrated solutions, in aromatic hydrocarbons, phenol must be therefore trimolecular. The simple ratio, $\text{concentration in hydrocarbon} / \text{concentration in water}$, gives constant values for acetone and trimethylamine, these substances not forming or forming but few double molecules. G. Y.

Molecular Weight of Salts in Indifferent Solvents. ARTHUR HANTZSCH (*Ber.*, 1905, 38, 1045—1048).—A solution of dimethylammonium chloride in chloroform is a non-electrolyte; molecular weight determinations were made with difficulty on account of its hygroscopic nature.

By the ebullioscopic method, dimethylammonium chloride was shown never to be unimolecular; in very dilute solution, it is trimolecular, and, with increasing concentration, tends to become quadrimolecular.

A. McK.

Theory of Colloids. II. JEAN BILLITZER (*Zeit. physikal. Chem.*, 1905, 51, 129—166).—The principles enunciated in the previous paper (*Abstr.*, 1904, ii, 18; see also *ibid.*, 19) are extended, and their application is tested by a large number of experiments. The relative charges of the colloids may be calculated from the amount of positive or negative ion carried down with each colloid from its solution, and the proportions of two colloids of opposite sign most favourable for their mutual precipitation should then be inversely as their charges (compare Biltz, *Abstr.*, 1904, ii, 324). This is confirmed quantitatively for ferric hydroxide (electropositive) and arsenious sulphide or antimonious sulphide (both electronegative). When the relative quantities of the two oppositely charged colloids are not those referred to, precipitation is incomplete and electrical transport experiments show that the liquid phase contains the colloid added in excess together with a small quantity of the other. Thus, with two colloids, as in the action of electrolytes on hydrosols, a certain minimum concentration must be reached before precipitation will take place. When a trace of gelatin is added to a solution of an electronegative colloid, precipitation by electrolytes is facilitated, that is, a smaller quantity of electrolyte effects precipitation; at the same time, it must be noted that gelatin in larger quantities hinders the precipitation even of an electronegative colloid (compare Neisser and Friedemann, *Abstr.*, 1904, ii, 546). The precipitation of an electropositive colloid in neutral or acid solution is in all cases hindered by gelatin.

With these observations is closely connected the fact that gelatin in neutral or acid solution is electropositive, whilst in alkaline solutions it is electronegative. It appears also that colloidal silicic acid is electronegative in alkaline and faintly acid solutions, but becomes electropositive with increasing acidity. When colloidal silicic acid has been precipitated by barium chloride and a trace of ammonia, the hydrogel is redissolved by hydrochloric acid; when the precipitation has been effected by potassium sulphate and hydrochloric acid, the hydrogel is redissolved by ammonia. Both these observations are associated with the amphoteric character of the silicic acid, which is electropositive or electronegative according to the electrolyte with which it is in contact. Similar observations may be made with such substances as methyl-orange, bismarck-brown, and eosin, which are weak electrolytes with large ions, and behave similarly to colloids in many respects. In all these cases, the hydrogel redissolves when its constituents (the colloid and the accompanying ion), which have originally had charges of opposite sign, become the same in sign through the influence of the added electrolyte.

The author deals on similar lines with the reversible and non-reversible precipitation of egg albumin, and with the phenomenon of agglutination.

J. C. P.

Pyridine as a Solvent and Ionising Medium for Inorganic Metallic Salts. JOHANNES SCHROEDER (*Zeit. anorg. Chem.*, 1905, 44, 1—36).—The behaviour of pyridine solutions of mercuric chloride, bromide, iodide, and cyanide, of silver nitrate, sulphate, cyanide, and thiocyanate, of cupric chloride, of ferrous chloride, and of ferric chloride respectively towards various reagents in the absence of water, and towards solutions of metallic salts in pyridine was examined. Mercuric salts combine with pyridine to form double salts of the type $\text{HgX}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$. The solubility of mercuric salts in pyridine increases in the sequence chloride, bromide, iodide, and cyanide. Molecular weight determinations of mercuric salts in pyridine, with the exception of mercuric chloride, give values which are too high. The tendency to form complex compounds increases in the sequence chloride, bromide, iodide, and cyanide.

Red mercuric sulphide is precipitated when hydrogen sulphide is passed into solutions of mercuric salts in pyridine. Mercury is deposited when stannous chloride is added to solutions of mercuric salts in pyridine. Mercuric chloride forms a double compound with ammonia and is completely precipitated from its pyridine solution by ammonia. Mercuric bromide undergoes a similar change, whilst the iodide is not entirely precipitated. Mercuric cyanide in pyridine solution does not form a double compound with ammonia.

Molecular weight determinations of silver salts dissolved in pyridine give values which are too high. Silver sulphide is formed when sulphur is added to solutions of silver salts in pyridine.

Ammonia forms the compound $\text{CuCl}_2 \cdot 4\text{NH}_3$ with cupric chloride in pyridine.

Ferrous chloride in pyridine solution is oxidised to ferric chloride by chlorine, bromine, or iodine. The molecular rise of the boiling

point for pyridine is 28.4. Molecular weight determinations of ferrous chloride in pyridine gave values which were too high.

In many cases, the reactions between dissolved salts and certain reagents took place in pyridine solution just as in water.

A. McK.

Kinetics of Reactions in Mixtures of Water and Alcohol.

ROBERT KREMANN (*Monatsh.*, 1905, 26, 279—313. Compare Skraup, *Abstr.*, 1894, i, 15; Gennari, *Abstr.*, 1896, ii, 413).—Contrary to Gennari's statement, the hydrolysis of alkyl acetates by sodium hydroxide, in absolute methyl or ethyl alcohol, is a bimolecular reaction and takes place completely. The rate of hydrolysis in methyl alcohol is about one-third of that in ethyl alcohol: the constant for the hydrolysis of ethyl acetate with sodium hydroxide in methyl alcohol, $k=0.00199$; in ethyl alcohol, $k=0.00540$; in propyl alcohol, $k=0.0213$; in *iso*amyl alcohol, $k=0.1153$. The presence of small quantities of water affects the rate of hydrolysis in methyl alcohol comparatively slightly; for ethyl acetate in 95 per cent. methyl alcohol, $k=0.0284$, whereas in ethyl, and still more in propyl, alcohol solution, the hydrolysis is greatly accelerated: in ethyl alcohol, $k=0.137$; in propyl alcohol, $k=0.439$.

As it is difficult to obtain perfectly anhydrous alcohol, it is possible that the greater rate of hydrolysis in the so-called absolute ethyl alcohol over that in absolute methyl alcohol is due to the presence of traces of water, and that in the perfectly anhydrous alcohols the contrary would be the case. It is to be considered also that in solutions of sodium hydroxide in alcohols there is an equilibrium between sodium, hydroxyl, and alkoxyl ions; the differences observed in the rates of hydrolysis in different alcohols may be due to differences in the concentrations of the alkoxyl ions.

In agreement with this, the constant of hydrolysis for ethyl acetate, with sodium methoxide in methyl alcohol, $k=0.00165$; with sodium ethoxide in ethyl alcohol, $k=0.00221$; with sodium propoxide in propyl alcohol, $k=0.00422$; with sodium *iso*amyloxide in *iso*amyl alcohol, $k=0.0333$. On the other hand, the constant of hydrolysis with sodium alkoxides is, in proportion to the rate of hydrolysis with sodium hydroxide, much smaller with amyl than with methyl alcohol as solvent; this was to be expected from the decrease in the electro-negative character of the alkoxyl ion with the increase in the molecular weight of the alcohol. When the concentration of the alkoxyl ions becomes extremely small in proportion to that of the hydroxyl ions, as in 50 per cent. or more dilute alcohols, the rates of hydrolysis of the same ester in different alcohols become approximately the same.

G. Y.

Kinetics of Reactions in Heterogeneous Systems. Hydrolysis in Non-homogeneous Systems. ROBERT KREMANN (*Monatsh.*, 1905, 26, 315—326. Compare Nernst, *Abstr.*, 1904, ii, 315).—The hydrolysis of ethyl benzoate by sodium hydroxide in absolute methyl alcohol and of amyl acetate by sodium hydroxide in absolute ethyl alcohol are bimolecular reactions. If the hydrolysis takes place in

aqueous solution, k , for ethyl benzoate, if calculated for a unimolecular reaction, remains constant throughout, whilst with amyl acetate the reaction is at first unimolecular, but towards the end becomes bimolecular. This change in the nature of the reaction, which is due to the mixture becoming homogeneous consequent on the high solubility of amyl acetate, is accompanied by the clearance of the solution.

G. Y.

Use of the Hot and Cold Tube in the Study of Chemical Reactions. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 905—914).—The author has extended the investigation, initiated by Sainte-Claire Deville, on the detection of reversible chemical reactions which occur only at high temperatures, by using tubes of fused silica, which can be cooled instantaneously from 1400° to the ordinary temperature by plunging them into cold water (compare this vol., ii, 316). The quantity of material used in each experiment was small, as the tubes had a mean capacity of 4 c.c., and were filled with gases under diminished pressure, about 40 mm.; the products of the reaction were therefore analysed eudiometrically (compare Abstr., 1889, 301), using reagents capable of detecting $1/500$ mg. of a substance. Seventeen experiments are described in the original, nine relating to chemical combination and eight to chemical dissociation; with one exception, namely, the union of diamond and oxygen at 1325° to form carbon monoxide and a little carbon dioxide, negative results were obtained in the first series of experiments; oxygen does not condense to ozone at high temperatures, oxygen, nitrogen, and water vapour do not form nitric acid, nor do carbon, graphite, or diamond combine directly with nitrogen or hydrogen. The second series of experiments included the effect of high temperatures on hydrocarbons, cyanogen, and the oxides of carbon: acetylene, methane, and naphthalene are decomposed into carbon and hydrogen (compare this vol., ii, 316), cyanogen is decomposed almost completely into graphite and nitrogen at 1425° , at 1400° the decomposition is slow, whilst at 1000° there is hardly any decomposition; carbon monoxide yields a small quantity of carbon and carbon dioxide at 1300 — 1325° (compare Abstr., 1891, 801), whilst carbon dioxide is quite stable at 1300 — 1325° .

M. A. W.

Addendum to the Sixth Report of the Committee [of the German Chemical Society] for Fixing Atomic Weights. HUGO ERDMANN (*Ber.*, 1905, 38, 978—979), HANS LANDOLT (*ibid.*, 1194).—In this Report, Erdmann was erroneously stated to have voted for the exclusive use of the table in which $H = 1$. He did not give a vote in favour of any course. Only one vote therefore was given in favour of the $H = 1$ table (compare this vol., ii, 155).

A. McK.

Construction of the Periodic System. ALFRED WERNER (*Ber.*, 1905, 38, 914—921).—The difficulty hitherto experienced of fitting the iron group and the metals of the rare earths into a periodic table of elements is attributed to undue compression of the table and to the attempt to multiply unimportant analogies. Taking into account only the leading characters of the elements, the author deduces a scheme in

which provision is made for eight periods. To the first and second periods, three elements each are allotted; the third and fourth periods have each eight elements (that is, $3 + 5$); the fifth and sixth periods have each eighteen elements (that is, $3 + 5 + 2 \times 5$); whilst to the seventh and eighth periods thirty-three elements each (that is, $3 + 5 + 2 \times 5 + 3 \times 5$) are allotted. It is shown that the mean difference between the atomic weights of two consecutive elements increases from the third period to the sixth, and on this basis the number of elements to be allotted to the other groups is estimated by extrapolation. The first period is so far hypothetical; the second, beginning with hydrogen and ending with helium, contains in all probability a third element not yet discovered. The third period begins with lithium and ends with neon; the fourth begins with sodium and ends with argon; the fifth begins with potassium and ends with krypton; the sixth begins with rubidium and ends with xenon; the seventh and eighth periods have many blanks, but the first member of the former is caesium, and the second member of the latter is radium. The extra elements inserted in the fifth and sixth periods as compared with the third and fourth, or in the seventh and eighth periods as compared with the fifth and sixth, are regarded as representing a sort of transition series for the elements between which they are inserted. Thus the metals of the rare earths are inserted in the seventh period between barium and the higher homologue of yttrium, and as the characters of these two elements do not markedly differ, the metals of the rare earths are necessarily very similar.

In arranging the elements according to the periodicity of their chemical properties, the author finds it necessary in four cases to invert the order of the atomic weights; thus, (1) argon comes before potassium, (2) cobalt comes before nickel, (3) tellurium comes before iodine, and (4) neodymium comes before praseodymium. It is noteworthy, however, that case (1) falls at the end of the fourth period, whilst case (3) occurs about the end of the sixth period; further, cases (2) and (4) occur 6—7 places later than cases (1) and (3) respectively. There is also considerable analogy between cobalt and nickel salts on the one hand, and neodymium and praseodymium salts on the other.

J. C. P.

Extraction Apparatus for Large Quantities of Vegetable Powders. C. E. JULIUS LOHMANN (*Chem. Zeit.*, 1905, 29, 365).—The apparatus consists of a slightly conical cylinder *A*, placed vertically, and provided at the top with a tubulure to which a condenser can be attached; at the bottom, it opens into a small bulb, *a*, and to this again is attached below a tap which terminates in a narrow tube, *b*; surrounding this tube is a wider tube, the side arm of which is connected with the shoulder of the cylinder *A*. A little dry cotton-wool is placed in *a*, the cylinder *A* is filled with 250—500 grams of the powder, and the apparatus attached by the lower tube to a 1500 c.c. flask. After opening the tap, the solvent is poured in from the top until the mass is quite saturated and the liquid begins to run through to the small, slightly drawn-out tube *b*. More solvent is then poured in until the flask is about one-third filled, the tap is closed, and, after connecting the

cylinder with a large condenser, the liquid is heated to boiling on a water-bath or sand-bath. The tap is easily regulated in such a manner that as much liquid runs through *b* as collects on the top ; at all events, the mass in *A* must be permanently covered with a layer of solvent. The colour of the liquid as it runs from *b* will generally show the progress of the extraction.

L. DE K.

Gas Holder with Constant Outflow. MARIO BETTI (*Chem. Zeit.*, 1905, 29, 219).—An arrangement is described whereby the outflow of gas from the ordinary gas holder is kept constant. The tube, which in the ordinary gas holder dips to the bottom, is replaced by two concentric tubes, soldered together in such a manner that they form a hydraulic valve, which regulates the flow of water into the gas holder, so that the pressure of the gas corresponds with a definite head of water.

A. McK.

Inorganic Chemistry.

Valency of Hydrogen. ROBERT DE FORCRAND (*Compt. rend.*, 1905, 140, 764—767).—The assumption that hydrogen is univalent is said to be difficult to harmonise with known facts. These can be more readily explained if hydrogen is assumed to be bivalent, in which case the valencies of all the elements will be doubled. The existence of subhaloid salts and suboxides ($\text{Ag}_2\text{F} + \text{Ag}_4\text{O}$), of compounds such as iodine trichloride and sulphur hexafluoride, of double salts such as those formed by the alkali haloids, and, in general, of the so-called molecular compounds, is referred to in support of the author's contention, and it is shown that simple graphic formulæ can be ascribed to a number of these compounds on the assumption of the bivalency of hydrogen.
H. M. D.

Precision attained in the Determination of the Atomic Weights of Hydrogen and Nitrogen. ANATOLE LEDUC (*Compt. rend.*, 1905, 140, 717—718).—The values obtained by the author for the atomic weights of hydrogen (compare Abstr., 1899, ii, 354) and nitrogen (compare Abstr., 1897, ii, 549) are in close agreement with the recent determinations of Guye, Mallet, Bogdan, Jaquerod, and Pintza (compare Abstr., 1904, ii, 392, 475, 557, 812).
M. A. W.

Atomic Weight of Iodine. ALBERT LADENBURG (*Annalen*, 1905, 338, 259—262).—A reply to Köthner's criticisms (compare following abstract, Abstr., 1903, ii, 360; 1904, ii, 556, and this vol., ii, 81).
K. J. P. O.

Atomic Weight of Iodine. PAUL KÖTHNER (*Annalen*, 1905, 338, 262—265).—A reply to Ladenburg (preceding abstract).
K. J. P. O.

Normal Basicity of Alkali Periodates. FEDERICO GIOLITTI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 217—220).—Periodic acid is monobasic towards sodium hydroxide when helianthin is used as indicator. By means of the electrometric method of Böttger (*Abstr.*, 1898, ii, 89), periodic acid is found to be dibasic. T. H. P.

Hydrogen Fluoride. I and II. ERNST DEUSSEN (*Zeit. anorg. Chem.*, 1905, 44, 300—340, 408—430).—Determinations of the strength of hydrogen fluoride by the action of its aqueous solutions in the inversion of cane-sugar showed that hydrofluoric acid is a weak acid: In concentrated solutions, it is somewhat stronger than chloroacetic acid; in the dilution of 1 mol. to 4 litres, both these acids are equally dissociated, whilst in more dilute solutions the dissociation of hydrogen fluoride increases more slowly than does the dissociation of chloroacetic acid. In the dilution of 1 mol. of hydrogen fluoride to 1000 litres, the acid is about half dissociated. Those results were also confirmed by determinations of electrical conductivity. Hydrogen fluoride has about the same strength as phosphoric acid; it is neither a definite monobasic nor a dibasic acid. The amount of hydrogen fluoride in an aqueous solution can be estimated by means of sodium or potassium hydroxides with phenolphthalein as indicator and with the use of conductivity water. Traces of sulphuric acid or of hydrofluosilicic acid are readily detected in solutions of hydrogen fluoride. By aid of the results quoted, the purity of any given sample of hydrofluoric acid may readily be determined.

Spohr's results on the inversion of sucrose by hydrofluosilicic acid are inaccurate. Polarimetric determinations of solutions containing hydrogen fluoride are readily made if the glass discs in the polarimetric tube are replaced by discs of fluorspar. At high temperatures, determinations may be made with tubes of platinum, fluorspar, or copper, although it is observed that platinum at elevated temperatures inverts a solution of sucrose to a slight extent.

According to the author's experience, the introduction of hydrofluoric acid into the sugar industry is likely to meet with little success.

An aqueous *N*/1 solution of commercial ammonium fluoride contained at 25° no measurable amount of hydrogen ions.

Hydrofluoric acid is recommended for freeing iron materials from rust.

By the action of concentrated hydrofluoric acid on an excess of copper oxide, a sparingly soluble oxyfluoride is produced.

For the separation of much aluminium oxide from little ferric oxide, fusion with hydrogen potassium fluoride is recommended.

The titration of ferrous iron by permanganate is inexact in the presence of hydrofluoric acid. A. McK.

Preparation of Oxygen. GEORGE F. JAUBERT (D.R.-P. 157171).—Oxygen may be obtained from bleaching powder in the cold by the simultaneous action of a ferrous or manganous salt and a copper, nickel, or cobalt salt. No decomposition of the hypochlorite is effected by iron, manganese, or copper salts alone. The bleaching powder is best mixed to a cream with water, and the most favourable results

are then obtained by adding ferrous and copper sulphates. The reaction may be carried out under pressure if required. The oxygen obtained is pure and free from chlorine. C. H. D.

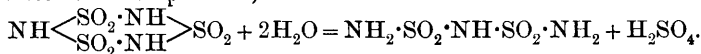
Solubility of Sulphur in Benzyl Chloride and some Properties of these Solutions. JOSEF JURI VON BOGUSKI (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 92—99).—Sulphur dissolves in benzyl chloride, and on cooling a hot saturated solution the sulphur separates in rhombic crystals. The solubility of the sulphur increases from 1 per cent. at 0° to 55·8 per cent. at 134°. In benzyl chloride, sulphur melts at 106·2—106·8° and does not mix with the excess of solvent, but above 136° sulphur and benzyl chloride mix in all proportions. Solubility curves and tables are given. T. H. P.

Composition of the Lime, Sulphur, and Salt Wash. JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1905, **28**, 244—255).—Chiefly an investigation of the reactions taking place when a mixture of sulphur and calcium hydroxide is boiled for different periods with water and salt. The sulphur in its various combinations was estimated by the usual methods. The free sulphur extracted by carbon disulphide was converted into potassium sulphate by boiling with potassium hydroxide with addition of hydrogen peroxide (Avery's process). Sodium chloride has no influence on the reaction between sulphur and calcium hydroxide. For the technical details, the original article should be consulted.

L. DE K.

Apparatus for preparing Liquid Sulphur Dioxide. BÉLA KRÉCSEY (*Chem. Zeit.*, 1905, **29**, 310).—An elongated glass vessel holding about 100—150 c.c. is furnished with a gas delivery tube reaching to the bottom of the reservoir and an exit tube; each tube is provided with a tap. The vessel is surrounded by a freezing mixture composed of salt and snow and a current of sulphur dioxide is admitted. As soon as a convenient quantity of this has condensed, both taps are closed and the apparatus is put into a cold place. If a current of sulphur dioxide is wanted at the lecture table, the exit tube is opened, but if some of the liquid is required, the tap of the inlet tube is turned. L. DE K.

New Products from the Action of Ammonia on Sulphuryl Chloride. ARTHUR HANTZSCH and BERNHARD C. STUER (*Ber.*, 1905, **38**, 1022—1043. Compare this vol., i, 317).—Trisulphimide is not known in the solid form. Indications of its transient formation in anhydrous solvents, such as ethyl acetate, were noted. The product previously described by Hantzsch and Holl (*Abstr.*, 1902, ii, 14) as trisulphide is *iminosulphonamide*, $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}_2$, produced by the action of water on trisulphimide, thus:

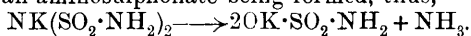


In the preparation of iminosulphonamide, silver trisulphimide is decomposed by anhydrous hydrogen cyanide and not by hydrogen sulphide, as formerly effected by Hantzsch and Holl (*loc. cit.*), whilst

ethyl acetate is used as the crystallising agent. Iminosulphonamide is readily decomposed at 0° by water, thus, $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{SO}_2 \cdot \text{NH}_2 + \text{H}_2\text{O} = \text{SO}_2(\text{NH}_2)_2 + \text{OH} \cdot \text{SO}_2 \cdot \text{NH}_2$, sulphonamide and aminosulphonic acid being formed. The electric conductivity of aqueous solutions of iminosulphonamide gives values corresponding with those for aminosulphonic acid, the sulphonamide also produced by the action of water on iminosulphonamide not being an electrolyte. Iminosulphonamide is moderately stable towards alkalis; it acts as a monobasic acid, forming salts of the type $\text{S}_2\text{H}_4\text{O}_4\text{N}_3\text{M}$. The ammonium salt,



was prepared. When iminosulphonamide is gradually added to an excess of an aqueous solution of alkali, the salt first formed gradually decomposes, one-third of the total nitrogen being evolved as ammonia and an aminosulphonate being formed, thus,



It is not certain, however, whether the metal is attached to nitrogen in the formulæ of such alkali salts.

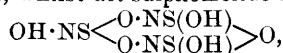
Silver iminosulphonamide, $\text{NAg}(\text{SO}_2 \cdot \text{NH}_2)_2, 1\frac{1}{2}\text{H}_2\text{O}$, prepared by the addition of iminosulphonamide to an excess of silver carbonate or of silver oxide suspended in water, is not acted on by cold concentrated aqueous potassium hydroxide with the formation of ammonia; it separates from a mixture of ether and pyridine in stellate crystals. When acted on by acids, it forms molecular amounts of aminosulphonic acid and sulphonamide. It is formed in small amount during the preparation of silver trisulphimide. It is sometimes formed in rhombohedra (possibly a second modification of the salt).

The gelatinous product obtained by Hantzsch and Holl (*loc. cit.*) by the action of ammonia on sulphuryl chloride in solution in light petroleum is difficult to free completely from ammonium chloride, and is probably *ammonium aci-sulphomelide*, $\text{S}_3\text{O}_3\text{N}_3(\text{ONH}_4)_3$.

Barium aci-sulphomelide, $(\text{S}_3\text{O}_6\text{N}_3)_2\text{Ba}_3, 5\text{H}_2\text{O}$, is easily soluble in strong acids, sulphomelide being formed.

Cyamelide is formed when dry ammonia is passed into a solution of carbonyl chloride in light petroleum at 0° , no melanurenic acid being produced.

Whilst cyamelide does not form salts, sulphomelide has been obtained only in the form of its salts. The constitution of sulphomelide is discussed in comparison with that of cyamelide (compare this vol., i, 331). The formula $\text{NH}:\text{SO} \begin{smallmatrix} \text{O} \cdot \text{SO}(\text{NH}) \\ \text{O} \cdot \text{SO}(\text{NH}) \end{smallmatrix} \text{O}$ is assigned to sulphomelide, whilst *aci-sulphomelide* has the formula



the former being the *pseudo*-acid and the latter the true acid.

Just as trisulphimide is more easily decomposed than cyanuric acid, sulphomelide is more readily decomposed than cyamelide.

A. McK.

Constitution of some Nitrogen Sulphonic Acids. ARTHUR HANTZSCH (*Ber.*, 1905, 38, 1043—1044).—The author does not agree with certain conclusions of Haga and of Divers respecting the con-

stitution of several sulphonic acids containing nitrogen (compare Hantzsch and Semple, *Abstr.*, 1896, ii, 95 ; Haga, *Proc.*, 1903, 19, 281 ; Divers, *Proc.*, 1903, 19, 283 ; *Trans.*, 1895, 67, 1098). A. McK.

Pure Nitrogen from Nitrous and Nitric Oxides and Ammonia. GREGORY PAUL BAXTER and CHARLES H. HICKEY (*Amer. Chem. J.*, 1905, 33, 300—304).—Pure nitrogen can be readily obtained in large quantities by the interaction of nitric or nitrous oxide and ammonia at a high temperature. In the case of nitric oxide, the following method is employed. The gas, generated by the action of nitric acid of sp. gr. 1.2 on copper turnings, is led through a wash-bottle containing strong ammonia solution, and afterwards over hot copper gauze or thoroughly platinised asbestos. The nitrogen thus obtained is passed through dilute sulphuric acid, and afterwards over fused potassium hydroxide, through a tower containing glass beads moistened with strong sulphuric acid, and finally through a small tube containing a roll of red-hot copper gauze. It is found that the sp. gr. of ammonia solution used for this purpose must not be higher than 0.92.

In the case of nitrous oxide, the gas obtained by heating ammonium nitrate is passed over red-hot platinised asbestos, then into a wash-bottle containing strong ammonia solution, and again over heated platinised asbestos. The purification of the nitrogen is effected as in the former case. E. G.

Synthetical Preparation of Ammonia. WESTDEUTSCHE THOMASPHOSPHAT-WERKE, G.M.B.H. (D.R.-P. 157287).—The synthetical preparation of ammonia from nitric oxide and hydrogen in the presence of platinum black according to the equation $2\text{NO} + 5\text{H}_2 = 2\text{NH}_3 + 2\text{H}_2\text{O}$ has not hitherto been possible on a technical scale, the presence of carbon monoxide in the Dowson gas or water-gas used leading to the production of ammonium formate. When, however, the temperature is kept below 80° by artificial cooling, ammonia is obtained. The reaction is greatly accelerated by the influence of the dark electric discharge, and a suitable apparatus for the purpose is described. C. H. D.

Electrolytic Oxidation of Ammonia. ERICH MÜLLER and FRITZ SPITZER (*Ber.*, 1905, 38, 1188—1190).—Polemical. A reply to Traube (this vol., ii, 242). A. McK.

Electrolytic Reduction of Nitrates to Nitrites. ERICH MÜLLER and FRITZ SPITZER (*Ber.*, 1905, 38, 1190—1194. Compare *Abstr.*, 1904, ii, 116).—In the electrolytic reduction of nitrates to nitrites, it is convenient to use cathodes coated with spongy copper, and for this purpose the copper ammonium salt is added to the alkaline solution ; small amounts of copper are accordingly precipitated in the course of the electrolytic reduction.

The authors have examined the question as to the concentration of the nitrite when the latter is reduced to ammonia to such an extent

as to render the production of nitrite from nitrate of no commercial value.

In the experiments quoted, varying amounts of sodium nitrite were added to solutions of sodium nitrate, and, after the current had passed for a certain time, the alteration of the amount of nitrite in the solution estimated. The irregular results obtained indicated that small amounts of some compound influenced the reduction. In certain cases, the nitrite used contained lead.

In order to ensure that the nitrite is not oxidised to nitrate, the concentration of hydroxyl ions in the solution is maintained at a definite value, no diaphragm being used.

A. McK.

Preparation of Yellow Arsenic by means of the Electric Arc. ALFRED STOCK and WERNER SIEBERT (*Ber.*, 1905, 38, 966—968).—A solution of the yellow variety of arsenic (compare this vol., ii, 25, and Erdmann and Unruh, *Abstr.*, 1903, ii, 73) is most readily prepared by passing a current of about 12 amperes between a carbon anode and a cathode consisting of an alloy of equal parts of arsenic and antimony, both electrodes being immersed in carbon disulphide contained in a vessel surrounded and covered by water and ice, the arsenic under these conditions dissolving in the carbon disulphide in the form of the yellow modification, whilst the antimony is disintegrated but does not enter into solution. After a sufficient quantity has dissolved, the carbon disulphide is separated from the water and filtered, and may be concentrated by distillation.

W. A. D.

Use of Arsenic Oxide in the Catalysis of Sulphur Trioxide. ERNST BERL (*Zeit. anorg. Chem.*, 1905, 44, 267—299).—The author has investigated the velocity of the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$, where arsenic oxide was used as the catalyst.

At temperatures ranging from 300° to 500°, glass is attacked by sulphur trioxide. The observation of Lunge and Reinhardt (*Abstr.*, 1904, ii, 724) that arsenic oxide is as good a catalyst as ferric oxide is confirmed; its catalytic power at first diminishes and then attains to a constant value. Mixtures of sulphur dioxide and oxygen were partially dried by sulphuric acid and the amount of moisture best suitable for the action was estimated. When the gases were dried by phosphoric oxide, the velocity of the reaction was diminished and became less the longer the drying was conducted. The presence of too much water in the mixture of gases dried by sulphuric acid is more harmful than prolonged drying with phosphoric oxide. The reaction proceeds in two stages, the first a process of diffusion and the second the process of chemical union (Nernst and Brunner). The determination of the temperature-coefficients gave within the temperatures examined, namely, 310° to 510°, the value 1.4 to 1.1 for every 10° rise of temperature, whereby the process of diffusion appears to proceed more slowly than the process of union. Sulphur trioxide exerts a strong inhibiting effect on the velocity of the action. Carbon dioxide has a similar effect. The presence of an excess of either of the reacting gases increases the rate of combination.

A. McK.

Preparation of Silicides, Borides, Aluminides, &c. EDWARD JÜNGST and RUDOLF MEWES (D.R.-P. 157615).—Difficultly fusible metallic haloids, such as calcium or barium chloride or fluoride, magnesium chloride, or potassium chloride, are fused in an electric furnace with such metals or non-metallic elements as form volatile haloid compounds with development of heat. Silicon, boron, aluminium, iron, phosphorus, chromium, and tin are available for this purpose; carbon cannot be employed, its chloride being endothermic. Thus calcium chloride and silicon yield calcium silicide and silicon tetrachloride; calcium chloride and iron yield calcium ferride and ferrous chloride.

C. H. D.

Use of Quartz Vessels in the Laboratory. FRANZ MYLIUS and ADOLF MEUSSER (*Zeit. anorg. Chem.*, 1905, 44, 221—224).—Quartz vessels are not acted on by water at temperatures up to 100°; the electrical conductivity remaining unaltered. The action of various alkalis was examined. Barium silicate was formed by the action of baryta water in the absence of air on a quartz vessel, maintained at 18° for six months. Dilute acids, with the exception of hydrofluoric acid, do not appreciably attack quartz vessels at temperatures up to 100°. Concentrated sulphuric acid at 18° and at 100° has no appreciable action. Phosphoric acid at 400° has a strong corroding action. The quartz vessels absorb certain dyes from their solutions.

The use of quartz vessels is recommended for physical or analytical work where neutral or aqueous acid solutions are dealt with.

A. McK.

Vessels of Fused Silica—their Use in Chemistry. Permeability of Vessels of Fused Silica. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 817—820, 821—825).—Details of the methods of manipulation of fused silica tubes are communicated in the first paper. In the second, experiments are described which show that fused silica is permeable to oxygen, nitrogen, and hydrogen at a temperature of 1300°. In one such experiment, a tube of 4 c.c. capacity was filled with pure oxygen at a pressure of half an atmosphere, the tube being then sealed and heated at 1300° for an hour and a half. After cooling, the tube was found to contain 3 c.c. of nitrogen. Another tube of 5 c.c. internal volume was filled with hydrogen at a pressure of one-fifth of an atmosphere and heated at 1300° for one hour. The gas extracted from the tube after the experiment consisted of 0.68 c.c. of hydrogen and 0.12 c.c. of nitrogen, measured at atmospheric pressure. A considerable amount of hydrogen has thus escaped from the tube, the original volume measured at atmospheric pressure being equal to 1.0 c.c. When naphthalene was heated in an exhausted fused silica tube at 1300°, carbon was deposited, and the hydrogen escaped almost completely through the walls of the tube. The volume of gas contained in the tube after heating for one hour at 1300° was only 0.18 c.c. (instead of 14 c.c. if all the hydrogen in the naphthalene had been liberated and retained), and analysis showed this to consist of 0.15 c.c. of hydrogen and 0.03 c.c. of nitrogen. Phenomena of the

same nature were observed when methane was heated in a fused silica tube.
H. M. D.

Silicic Acid. III. EDUARD JORDIS (*Zeit. anorg. Chem.*, 1905, **44**, 200—208. Compare Abstr., 1903, ii, 364, 475).—It is impossible to obtain pure silicic acid in the hydrosol form. The only silicic acid which can be obtained pure is the solid. Attempts to prepare a pure hydrogel of silicic acid are described.
A. McK.

Solubility of Potassium Chloride, Bromide, and Iodide in Water. ADOLF MEUSSER (*Zeit. anorg. Chem.*, 1905, **44**, 79—80).—The solubility of potassium chloride, bromide, and iodide respectively in water was determined from temperatures about 10° to the eutectic point.
A. McK.

Composition of an Ancient English Gunpowder. LOYS DESVERGNES (*Ann. Chim. anal.*, 1905, **10**, 102—103).—A bomb found among débris in Saint Martin de Ré (France), and probably used by the English besieging army in 1627, contained a moist powder which, after drying and allowing for the 17·2 per cent. of rust it contained, consisted of nitre 38·5, sulphur 23·5, and charcoal 38 parts. A former English gunpowder consisted of nitre 75 parts, sulphur 10 parts, and charcoal 15 parts. If, like the above specimen, such a sample has been subjected to leaching until only 38·5 of nitre remains, the sulphur and charcoal would then have become respectively 24·5 and 37, which are practically the figures found.
L. DE K.

Sodamide. FRITZ EPHRAIM (*Zeit. anorg. Chem.*, 1905, **44**, 185—199).—A study of the action of sodamide on inorganic substances. When sodamide is added to a solution of sulphur in xylene and the mixture heated, ammonia, nitrogen, sodium, and ammonium polysulphides and a substance rich in nitrogen are formed. When bromine is added to benzene containing sodamide in suspension, the action is represented by the equation $4\text{NaNH}_2 + 3\text{Br}_2 = 4\text{NaBr} + \text{N}_2 + 2\text{NH}_4\text{Br}$. The reaction proceeds less vigorously when iodine is substituted for bromine. Sodamide acts vigorously on magnesium, hydrogen being evolved and a mixture of magnesium nitride and sodium being produced. Sodamide has no action on iron, tin, copper, and silver.

A number of oxides were heated with sodamide. Lead monoxide was reduced to lead; copper oxide and cadmium oxide were also reduced. With mercuric oxide, an amalgam was formed. Antimony trioxide gave sodium antimonite and antimony. Reduction also took place with arsenic trioxide, chromic anhydride, chromium trioxide, ferric oxide, manganese sesquioxide, manganous oxide, zinc oxide, tungstic acid, and vanadium pentoxide.

Lead sulphide was reduced to lead and copper sulphide to copper. Bismuth sulphide yielded an alloy of bismuth and sodium. The action on antimony sulphide, arsenic sulphide, copper sulphate, lead sulphate, and sodium sulphate was also examined.

The chlorides of lead, mercury, silver, tin, zinc, and barium were also reduced to the corresponding metals. Calcium chloride and potassium chloride did not act on sodamide.

Copper phosphate was reduced to copper and ferric phosphate to iron.

When lead nitrate and sodamide were rubbed together in a mortar, the mixture deflagrated; the action with silver nitrate was similar. Bismuth nitrate, when heated with sodamide, formed an alloy.

A mixture of potassium chlorate and sodamide exploded when heated. Lead borate yielded lead. Ferric hydroxide, cadmium hydroxide, and other metallic hydroxides were converted into the corresponding oxides. A. McK.

Sodium Hyposulphite. ARTHUR BINZ (*Zeit. Farb. Text. Ind.*, 1905, 4, 161—162).—When turmeric paper, moistened with a slightly alkaline solution of sodium hyposulphite, is exposed to the air, it loses the brown colour due to the alkali without bleaching taking place. It appears that an acid salt is formed, a fact which is more readily explained by assuming Bernthsen's equations: (1) $\text{Na}_2\text{S}_2\text{O}_4 + \text{O} = \text{Na}_2\text{S}_2\text{O}_5$; (2) $\text{Na}_2\text{S}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{NaHSO}_3$, than by accepting Schützenberger's formula for sodium hyposulphite. The structure of the latter substance is discussed at some length (compare Bernthsen, this vol., ii, 240; Bazlen, *ibid.*, ii, 240; Reinking, Dehnel, and Labhardt, *ibid.*, i, 261). W. A. D.

Preparation of Hyposulphites. M. BILLY (*Compt. rend.*, 1905, 140, 936—937).—The author finds that sodium hyposulphite cannot be prepared by the action of sulphur dioxide on sodium in the presence of a neutral solvent such as ether or light petroleum (compare Badische Anilin- & Soda-Fabrik, Abstr., 1904, ii, 250); in the presence of absolute alcohol, however, both sodium and magnesium are readily converted into the corresponding hyposulphite by the action of sulphur dioxide; it is probable that traces of the metallic ethoxide and hydride are first formed; the latter reacts with the sulphur dioxide to form the hyposulphite regenerating hydrogen, which converts a fresh portion of the metal into the hydride (compare Moissan, Abstr., 1903, ii, 75). The formation of Nabl's zinc hyposulphite is similarly explained (compare Abstr., 1900, ii, 13).

M. A. W.

Normal Sodium Thiophosphate, containing Water of Crystallisation. EMANUEL GLATZEL (*Zeit. anorg. Chem.*, 1905, 44, 65—78).—Normal sodium thiophosphate, $\text{Na}_3\text{PS}_4 \cdot 8\text{H}_2\text{O}$, prepared from sodium monosulphide, phosphorus pentasulphide, and water, forms transparent, monoclinic crystals, which are decomposed at the ordinary temperature by water, hydrogen sulphide being evolved. When the dry salt is heated, hydrogen sulphide is also evolved and a yellow mass remains. A. McK.

Absorption Compounds of Colloidal Silver and Other Inorganic Colloids with Organic Colloids. ALFRED LOTTER-MOSER (*J. pr. Chem.*, 1905, [ii], 71, 296—304).—For the preparation of colloidal silver, the isolation of protalbic or lysalbic acid is unnecessary, as the liquid hydrosol is formed by reduction of ammoniacal

silver nitrate solutions containing egg-albumin, serum-albumin, or casein. A colloidal silver, similar to Paal's preparation (Abstr., 1902, ii, 500), is formed by boiling an ammoniacal solution of silver nitrate and egg-albumin with sodium hydroxide. On addition of silver nitrate to a solution of starch in dilute sodium hydroxide, the hydrosol of silver oxide is formed; this is reduced to colloidal silver on prolonged boiling, or quickly on treatment with formaldehyde. The hydrosol so obtained is very stable and does not give a precipitate with nitric, sulphuric, or acetic acid; on addition of hydrochloric acid, a precipitate of silver and silver chloride is formed. The brown, solid hydrosol, precipitated by alcohol or by a large excess of glacial acetic acid, dissolves slowly in water. Liquid hydrosols are formed from aqueous silver nitrate, also by the action of alkaline dextrin, gelatin, agar-agar solutions, or powdered hide. Liquid and solid hydrosols of silver haloids are formed by the same reagents.

The liquid hydrosol, formed by heating starch with aqueous sodium hydroxide, reacts, after neutralisation with acetic acid, towards iodine in the same manner as does ordinary starch solution. The deep blue solid hydrosol, which is precipitated on addition of alcohol, loses iodine slowly when washed with alcohol or ether, and changes into a brown, granular substance, which contains iodine, as it dissolves in water to a blue solution. The blue colloid loses its colour when heated, and becomes blue again, not on cooling, but on solution in water.

G. Y.

Relationships between the Solubility of Calcium Sulphate and the Hydration of Gypsum and of Portland Cement. PAUL ROHLAND (*Zeit. angew. Chem.*, 1905, 18, 327—330).—The results obtained by Jones and Getman (Abstr., 1904, ii, 386) on the existence of hydrates in concentrated solutions of electrolytes throw light on the solubility of calcium sulphate at varying temperatures.

In determinations of the solubility of calcium sulphate in water, the size of the calcium sulphate particles is an important factor on which the rate of hydration of calcium sulphate is also dependent. The substance undergoing hydration must first pass into solution before hydration takes place. From the fact that both calcium sulphate semihydrate and anhydrous calcium sulphate first pass into solution before hydration occurs, the conclusion is drawn that, before the solubility product is exceeded, hydrated molecules are present in solution. Calcium sulphate exhibits even in dilute salt solutions a maximum which corresponds with a maximum of the rate of hydration.

A. McK.

Formation of Oceanic Salt Deposits. XLI. Temperature of Formation of Potassium Pentacalcium Sulphate. JACOBUS H. VAN'T HOFF, GERARDUS L. VOERMAN, and WALTER C. BLASDALE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 12, 305—310).—The formation of potassium pentacalcium sulphate according to the equation $K_2Ca(SO_4)_2 \cdot H_2O + 4CaSO_4 \cdot 2H_2O \rightleftharpoons K_2Ca_5(SO_4)_6 \cdot H_2O + 8H_2O$ has been previously described (Abstr., 1904, ii, 561), and the equilibrium temperature was found to lie between 83° and the ordinary temperature. Tensi-

metric observations gave the value 31.8° for the equilibrium temperature and 34.7 mm. for the equilibrium pressure. By the addition of tartaric acid, the temperature is lowered to -2.2° and the pressure to 2.87 mm., from which the pressure at other temperatures is calculable. A diagram illustrating the field of the pentasulphide is given; the field is small at 25° , but increases with rise of temperature.

L. M. J.

Action of Ultra-violet Light on Glass. FRANZ FISCHER (*Ber.*, 1905, **38**, 946—947).—Various kinds of glass have been exposed to ultra-violet rays from a quartz-mercury lamp, the short space between the quartz and glass being filled with hydrogen. Jena combustion glass, durax glass (Schott), German lead glass, and English lead glass were not affected, whereas ordinary Thuringian glass, apparatus glass from Greiner, apparatus glass from Bock and Fischer, and normal thermometer glass (Schott) were coloured strongly violet within 12 hours. All the latter contained manganese, whereas the glasses which were not discoloured were free from manganese.

The violet colour is readily destroyed by heating the glass until it softens.

J. J. S.

Complexity of Glucinum. CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1905, **27**, 233—237).—Pollok (*Trans.*, 1904, **85**, 1630) has stated that the beryl of Limoges contains a new element which resembles glucinum in its chemical properties but has a much higher equivalent.

The results of Pollok's experiments are discussed and it is suggested that they may have been produced by the presence of moisture, which causes a rapid decomposition of glucinum chloride with loss of chlorine. For this reason, the opinion is expressed that Pollok's results cannot be regarded as proving the existence of a new element in the beryl until it is shown that moisture was carefully excluded from the chloride used in his experiments.

E. G.

Alloys of Magnesium and Lead. G. GRUBE (*Zeit. anorg. Chem.*, 1905, **44**, 117—130).—The author has examined the curve of cooling of mixtures of magnesium and lead to see whether a compound is formed. The temperatures were determined by a thermo-element, of which the one wire consisted of platinum and the other of an alloy of platinum and rhodium.

Antimony melts at 620° , zinc at 412° , lead at 327° , and magnesium at 651° .

When varying weights of lead and magnesium are melted together, only one compound, PbMg_2 , is formed, provided that the temperature does not exceed 750° . This compound separates at 551.3° . The curve shows two eutectic points, where the percentage of lead is 67 and 97 respectively, corresponding with the temperatures 459.2° and 246.9° .

The compound is brittle, steel-blue in colour, and stable in dry air. In moist air, it is quickly decomposed to form a black powder, from which a hydrate corresponding with the formula $\text{PbO} \cdot 2\text{MgO} \cdot 3\text{H}_2\text{O}$ is produced.

A. McK.

Zinc Chloride. Solubility of Salts. XIV. FRANZ MYLIUS and RUDOLF DIETZ (*Ber.*, 1905, 38, 921—923. Compare Dietz, *Abstr.*, 1899, ii, 221).—Zinc chloride has been obtained in the anhydrous and in five hydrated modifications, containing 1, $1\frac{1}{2}$, $2\frac{1}{2}$, 3, and 4 H_2O respectively. The existence of a hydrate containing $2\text{H}_2\text{O}$ is not confirmed. The solubility curve consists of seven branches, the progressive conversion of the anhydrous salt into its hydrates is reversible. A 52 per cent. solution of zinc chloride does not solidify at -62° , whilst at 75.5° the solution yields a eutectic mixture which melts at 0° ; concentrated solutions form a brittle, glassy mass when strongly cooled. Seven different systems, in which the saturated solutions contain 67.5—81 per cent. of zinc chloride, are capable of existence at 0° ; at this temperature, a transition from one form to another containing more water of crystallisation is accompanied by a diminution in the concentration of the saturated solution, by an increase in the solubility of the crystalline substance, and by a diminution of the excess of the solvent over the water of crystallisation of the solute. G. Y.

Revision of the Atomic Weight of Cadmium. Analysis of Cadmium Chloride. GREGORY P. BAXTER and MURRAY A. HINES (*J. Amer. Chem. Soc.*, 1905, 27, 222—231).—The cadmium chloride used in these experiments was prepared in the following manner. Cadmium sulphide, prepared by fractional precipitation, was converted into the nitrate, and the nitrate into the sulphate. The sulphate was submitted to electrolysis, the cadmium thus obtained was dissolved in pure hydrochloric acid, and the chloride was converted into the double ammonium salt. The cadmium ammonium chloride was purified by fractional crystallisation, two fractions of pure material being thus obtained. A third sample of material used in the analyses was a portion of that employed in the determination of the sp. gr. of cadmium chloride (*Abstr.*, 1904, ii, 257). Each of these specimens was converted into cadmium chloride by ignition in a current of dry hydrogen chloride.

In the first series of analyses, the ratio of cadmium chloride to silver chloride was determined by the addition of a slight excess of silver nitrate to a solution of the cadmium salt, the precipitated silver chloride being collected, washed, dried, and weighed; the silver chloride dissolved in the washings was estimated by precipitating it with excess of silver nitrate, the precipitate produced being compared by means of the nephelometer (Richard and Wells, *Abstr.*, 1904, ii, 287) with that yielded by standard solutions of hydrochloric acid.

In a second series of experiments, the weight of pure silver required to combine exactly with the chlorine in cadmium chloride was determined by dissolving a weighed quantity of pure silver in nitric acid and adding the diluted solution to that of the cadmium chloride. Portions of the solution were tested from time to time in the nephelometer for excess of chlorine or silver and, if necessary, standard silver nitrate or hydrochloric acid was added until the amounts of chlorine and silver in the solution were equivalent.

The value for the atomic weight of cadmium obtained as the average result of the first series, consisting of three experiments, was 112.476,

whilst the average of the six determinations of the second series was 112.462, the average of the whole of the results being 112.469 ($\text{Ag} = 107.93$; $\text{Cl} = 35.473$). E. G.

Preparation and Properties of Manganese Boride. EDGAR WEDEKIND [and K. FETZER] (*Ber.*, 1905, **38**, 1228—1232).—A crystalline regulus containing about 82 per cent. of manganese is formed when boron and manganese thermite are brought together and the mixture ignited with magnesium powder (Goldschmidt process). The small excess of manganese and boron is removed as chloride by heating the powdered mass in a stream of chlorine and washing quickly with ice-cold water. The greyish-black, glistening, crystalline *manganese boride*, MnB_2 , contains 71.7 per cent. of manganese; it is slowly decomposed by water and dilute acids and has a sp. gr. 6.04 at 19° .

A manganese boride, MnB , containing 82.2 per cent. of manganese, very similar to the above in appearance and properties, is obtained on heating manganese suboxide and boron in the electric furnace (compare Binet du Jassoneix, this vol., ii, 90). E. F. A.

Oxidation of Metals in the Cold in presence of Ammonia. CAMILLE MATIGNON and G. DESPLANTES (*Compt. rend.*, 1905, **140**, 853—855).—The metals in finely divided condition were shaken up at the ordinary temperature in large flasks containing 10 c.c. of ammonia solution (255 grams per litre) for periods varying from 24 to 60 hours. In the majority of cases, blank experiments were made in which the metals were similarly shaken with distilled water.

In the presence of ammonia, nickel, cobalt, silver, cadmium, zinc, molybdenum, tungsten, and mercury are oxidised; with tin and chromium, no action takes place. H. M. D.

Dibromotetra-amminecobalt Salts. ALFRED WERNER and A. WOLBERG (*Ber.*, 1905, **38**, 992—998).—Dibromotetra-amminecobalt bromide, prepared by the action of fuming hydrobromic acid on carbonatotetra-amminecobalt bromide according to the equation $[\text{CO}_3:\text{Co}(\text{NH}_3)_4]\text{Br} + 2\text{HBr} = \text{H}_2\text{O} + \text{CO}_2 + [\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{Br}$, is a green, amorphous solid.

Dibromotetra-amminecobalt chloride, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$, prepared by the action of concentrated hydrochloric acid on the bromide, forms glistening, green, prismatic needles, the aqueous solution of which quickly changes at the ordinary temperature into the corresponding aquo-salt, thus, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{Cl} + \text{H}_2\text{O} = [\text{Br}(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{ClBr}$, the aqueous solution of which is reddish-violet. The *iodide*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{I}$,

prepared by the action of potassium iodide on the preceding salt, forms greenish-brown needles; the formation of the corresponding aquo-salt proceeds slowly. The *platinichloride*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]_2\text{PtCl}_6$, and the *aurichloride*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{Cl} \cdot \text{AuCl}_3$, were prepared.

The *sulphate*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]_2\text{SO}_4$, prepared by the action of dilute sulphuric acid on the dibromochloride, forms light green crystals, which are readily acted on by water to form the aquo-salt. Whilst in the dichloro-series a hydrogen sulphate only has been isolated

having the formula $[\text{Cl}_2\text{Co}(\text{NH}_3)_4]\text{SO}_4\text{H}$, in the dibromo-series the normal salt is formed.

The *nitrate*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{NO}_3$, forms bright green prisms. The *dichromate*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]_2\text{Cr}_2\text{O}_7$, forms yellowish-green plates. The *thiocyanate*, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{CNS}$, forms green crystals.

The dibromo-salts described form green solutions with water, which are rapidly changed, first into bromoaquotetra-aminocobalt salts, and then into diaquo-salts, thus, $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{Br} + \text{H}_2\text{O} =$

$$\begin{array}{c} [\text{BrCo}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Br}_2 \\ \text{and } [\text{BrCo}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Br}_2 + \text{H}_2\text{O} = [\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]\text{Br}_3. \end{array}$$

These transformations may be studied by determinations of the variation of the electrical conductivity of the solutions. A. McK.

Saturated Series of Dicobaltammine Compounds. ALFRED WERNER and R. FEENSTRA (*Ber.*, 1905, **38**, 923—925).—The cobalt-ammines richest in ammonia have the formula $[\text{Co}(\text{NH}_3)_6]\text{X}_3$. In addition to these simple compounds, other saturated derivatives containing more than one atom of cobalt and of the general type $\text{X}_2[\text{Co}(\text{NH}_3)_5 \cdot \text{NH} \cdot \text{Co}(\text{NH}_3)_5]\text{X}_2$ have been prepared.

Iminodipyridineoctamminedicobalt chloride,



is obtained by warming dichloroaquotriamminocobalt chloride with water and pyridine. The yield is small and appears to vary considerably; on treatment with concentrated hydrobromic acid, the corresponding *bromide* is obtained; this forms large, glistening, brownish-yellow needles containing $2\text{H}_2\text{O}$. J. J. S.

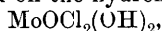
Hexahydroxylaminecobalt Salts. ALFRED WERNER and E. BERL (*Ber.*, 1905, **38**, 893—899. Compare Feldt, *Abstr.*, 1894, ii, 187).—Hexahydroxylaminecobalt chloride, $[\text{Co}(\text{NH}_2 \cdot \text{OH})_6]\text{Cl}_3$, formed by the action of hydroxylamine hydrochloride on dichlorodiethylenediaminecobalt chloride or on chlorohydroxylaminediethylenediaminecobalt chloride in aqueous potassium hydroxide solution, crystallises in large, golden leaflets, darkens on exposure to light, and yields cobalt chloride when boiled with acetic anhydride. With potassium ferrocyanide in aqueous solution, the chloride forms a reddish-brown, crystalline precipitate, which decomposes on exposure to light; with sodium acetate a yellow, crystalline precipitate, with potassium ferricyanide a brown, amorphous precipitate, and with sodium carbonate and with hydriodic acid yellow, unstable precipitates are formed. With hydrobromic acid in aqueous solution, hexahydroxylaminecobalt chloride forms the yellow, crystalline *bromide*; with ammonium oxalate the yellow, crystalline *oxalate*, with nitric acid the *nitrate* which crystallises in long, yellow needles, with sulphuric acid the yellow *sulphate*, $[\text{Co}(\text{NH}_2 \cdot \text{OH})_6]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, which decomposes at $90\text{--}100^\circ$, and with potassium cyanide a yellow, unstable *cyanide* are formed.

G. Y.

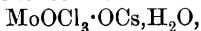
Chlorinated and Brominated Molybdates, Brominated Molybdites, and their Corresponding Acids. RUDOLF F. WEINLAND and W. KNÖLL (*Zeit. anorg. Chem.*, 1905, **44**, 81—116. Compare

Abstr., 1904, ii, 263; this vol., ii, 326).—Since oxygen in molybdates can be replaced by sulphur, it can also be replaced by chlorine or by bromine.

Trichloromolybdic acid, $\text{MoOCl}_3 \cdot \text{OH} \cdot 7\text{H}_2\text{O}$, prepared by the action of fuming hydrochloric acid on the hydroxychloride,



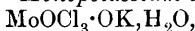
forms green prisms, from the solution of which in water molybdic acid does not separate. *Dicæsium tetrachloromolybdate*, $\text{MoCl}_4(\text{OCs})_2$, prepared from the hydroxychloride, $\text{MoOCl}_2(\text{OH})_2$, and cæsium chloride, forms green, hygroscopic crystals, from the aqueous solution of which molybdic acid separates. *Monocæsium trichloromolybdate*,



forms greenish-yellow, hygroscopic crystals. *Cæsium hydrogen chlorotrimolybdate*, $\text{Mo}_6\text{O}_{11}\text{Cl}_{14} \cdot \text{Cs}_2\text{O} \cdot 22\text{H}_2\text{O}$, forms hygroscopic prisms.

Dirubidium tetrachloromolybdate, $\text{MoCl}_4(\text{ORb})_2$, forms tetragonal plates. *Monorubidium trichloromolybdate*, $\text{MoOCl}_3 \cdot \text{ORb} \cdot \text{H}_2\text{O}$, forms hard crystals.

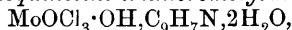
Dipotassium tetrachloromolybdate, $\text{MoCl}_4(\text{OK})_2 \cdot 2\text{H}_2\text{O}$, forms greenish-yellow, hexagonal plates. *Monopotassium trichloromolybdate*,



forms hexagonal plates. *Potassium hydrogen chlorotrimolybdate*, $\text{Mo}_6\text{O}_{11}\text{Cl}_{14} \cdot \text{K}_2\text{O} \cdot 6\text{H}_2\text{O}$, crystallises in prisms.

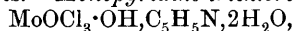
Diammonium tetrachloromolybdate, $\text{MoCl}_4(\text{ONH}_4)_2 \cdot 2\text{H}_2\text{O}$, forms hexagonal plates.

Diquinoline tetrachloromolybdate, $\text{MoCl}_4(\text{OH})_2 \cdot (\text{C}_9\text{H}_7\text{N})_2 \cdot 9\text{H}_2\text{O}$, forms rhombic plates. *Monoquinoline trichloromolybdate*,



separates from strong hydrochloric acid in colourless needles.

Dipyridine tetrachloromolybdate, $\text{MoCl}_4(\text{OH})_2 \cdot (\text{C}_5\text{H}_5\text{N})_2 \cdot 2\text{H}_2\text{O}$, crystallises in white leaflets. *Monopyridine trichloromolybdate*,



separates from hydrochloric acid in needles. *Hydrogen pyridine chlorotrimolybdate*, $\text{Mo}_3\text{O}_5\text{Cl}_7 \cdot \text{OH} \cdot \text{C}_5\text{H}_5\text{N} \cdot 10\text{H}_2\text{O}$, forms hygroscopic prisms, which on exposure gradually become blue. *Hydrogen pyridine chlorononmolybdate*, $\text{Mo}_9\text{O}_{17}\text{Cl}_{18}(\text{OH})_2 \cdot (\text{C}_5\text{H}_5\text{N})_2 \cdot 5\text{H}_2\text{O}$, forms tetragonal or hexagonal prisms.

Monoquinoline tribromomolybdate, $\text{MoOBr}_3 \cdot \text{OH} \cdot \text{C}_9\text{H}_7\text{N} \cdot 2\text{H}_2\text{O}$, prepared from the mixture of bromides containing quinquevalent and sexavalent molybdenum (obtained from the action of anhydrous hydrogen bromide on heated molybdic acid) by treating it with bromine and then adding quinoline hydrobromide, forms yellowish-white leaflets.

Dipyridine tetrabromomolybdate, $\text{MoBr}_4(\text{OH})_2 \cdot (\text{C}_5\text{H}_5\text{N})_2 \cdot 2\text{H}_2\text{O}$, forms yellow prisms.

Dibromomolybdous acid, $\text{MoBr}_2\text{O} \cdot \text{OH} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, forms dark brown, hygroscopic prisms. *Tetrabromomolybdous acid*, $\text{MoBr}_4 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$, forms hygroscopic needles.

Dicæsium pentabromomolybdite, $\text{MoBr}_5\text{OCs}_2$, forms glistening octahedra.

Dirubidium pentabromomolybdite, $\text{MoBr}_5\text{ORb}_2$, forms rhombic pyramids, which are sometimes dark red and sometimes yellowish-green.

Dipotassium pentabromomolybdate, MoBr_5OK_2 , forms dark red pyramids. *Monopotassium tetrabromomolybdate*, $\text{MoBr}_4\cdot\text{OK}, 2\text{H}_2\text{O}$, forms olive-green pyramids.

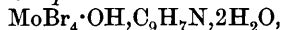
Diammonium pentabromomolybdate, $\text{MoBr}_5\text{O}(\text{NH}_4)_2$, forms reddish-brown octahedra.

Monolithium tetrabromomolybdate, $\text{MoBr}_4\text{OLi}, 4\text{H}_2\text{O}$, forms dark red, hygroscopic needles.

Magnesium pentabromomolybdate, $\text{MoBr}_5\text{OMg}, 7\text{H}_2\text{O}$, forms olive-green octahedra or hexagonal pyramids,

Calcium tetrabromomolybdate, $\text{Ca}(\text{MoBr}_4\text{O})_2, 7\text{H}_2\text{O}$, forms tetragonal plates.

Diquinoline pentabromomolybdate, $\text{MoBr}_5\text{OH}_2, (\text{C}_9\text{H}_7\text{N})_2, 2\text{H}_2\text{O}$, forms olive-green needles. *Monoquinoline tetrabromomolybdate*,



forms red needles.

Dipyridine pentabromomolybdate, $\text{MoBr}_5\text{OH}_2, (\text{C}_5\text{H}_5\text{N})_2$, forms green needles.

Monopyridine tetrabromomolybdate, $\text{MoBr}_4\cdot\text{OH}, \text{C}_5\text{H}_5\text{N}$, forms red needles.

When attempts were made to prepare a copper salt containing quinquevalent molybdenum, glistening, black needles of the compound $\text{CuBr}_3\text{H}, 10\text{H}_2\text{O}$ were obtained.

A. McK.

Properties of Tungsten Trioxide as a Ceramic Colouring Matter. ALBERT GRANGER (*Compt. rend.*, 1905, 140, 935—936).—The use of tungsten trioxide as a yellow colouring matter in enamels and glazes is limited by the fact that the colour is destroyed at high temperatures, the glaze becoming opaque. The author finds, however, that permanent yellow glazes can be obtained by fusing tungsten trioxide at 800° with lead silicate, with a mixture of zinc borate and silicate, or with bismuth oxide; whilst a glaze having the general formula $\text{MO}, 1.4\text{SiO}_2, 0.1\text{Al}_2\text{O}_3, 0.5\text{B}_2\text{O}_3, 0.1\text{WO}_3$, where M represents Na_2 , Ca, or Pb, is readily fusible, transparent, and yellow in colour.

M. A. W.

Sodium Hexatungstate. A. W. LEONTOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 130—141).—The author has been unable to prepare the sodium octotungstate described by Ullik (*Sitzungsber. Wien. Akad.*, 56, [ii], 157), but has obtained a sodium hexatungstate, $\text{Na}_2\text{W}_6\text{O}_{19}, 15\text{H}_2\text{O}$, which forms long crystals and may be recrystallised without decomposition.

T. H. P.

Perstannic Acids and Perstannates. SEBASTIAN TANATAR (*Ber.*, 1905, 38, 1184—1186).—Stannic acid, which had been precipitated from a solution of stannous chloride by sodium carbonate, was triturated with an excess of a 30 per cent. solution of hydrogen peroxide and the mixture heated at about 70° . After remaining for some days in a desiccator, a white, amorphous powder, $\text{HSnO}_4, 2\text{H}_2\text{O}$, was obtained. On further exposure in a desiccator, this acid slowly loses water and oxygen. It undergoes with water partial decomposition into stannic acid and hydrogen peroxide. When dried at 100° , it is

converted into the acid, $\text{H}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$. This is a more convenient method for preparing the latter than Spring's method is.

Potassium perstannate, $\text{KSnO}_4 \cdot 2\text{H}_2\text{O}$, prepared by the action of hydrogen peroxide on potassium stannate, is a white, amorphous powder, which, when heated, parts with oxygen and water. Its aqueous solution has an alkaline reaction; on the addition of sulphuric acid, it decolorises permanganate. When heated, it is converted into the salt, $\text{K}_2\text{Sn}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$.

Sodium perstannate, $\text{NaSnO}_4 \cdot 2\text{H}_2\text{O}$, prepared in a similar manner, is sparingly soluble in water, by which it is readily decomposed; it is a white, amorphous powder. A. McK.

Separation of Thorium from the Cerite Earths by means of Normal Sodium Sulphite. HERMANN GROSSMANN (*Zeit. anorg. Chem.*, 1905, 44, 229—236).—Normal sodium sulphite effects a quantitative precipitation of the tervalent cerite earths as normal sulphites, whilst thorium and zirconium salts, in the presence of an excess of the precipitant, form basic sulphites which are gelatinous and readily soluble. In the solution of the thorium salt, the existence of complex alkali thorium sulphites is assumed; the salt, $\text{Th}_2(\text{OH})_2(\text{SO}_3)_3 \cdot 2\text{Na}_2\text{SO}_3 \cdot 22\text{H}_2\text{O}$, was isolated as a solid, practically insoluble in water and readily soluble in dilute hydrochloric acid. The salt, $\text{Th}(\text{OH})_2\text{SO}_3 \cdot 2\text{K}_2\text{SO}_3 \cdot 10\text{H}_2\text{O}$, is a white, amorphous powder.

Chavastelon's method of separation cannot be applied when the amount of thorium present is small.

Normal ammonium sulphite precipitates dilute solutions of thorium nitrate as basic sulphite, whilst zirconium nitrate with an excess of sulphite gives a clear solution, from which gelatinous ammonium zirconium sulphite separates after 12 hours.

The more strongly basic cerite earths do not tend to form alkali double sulphites. The solubility of the hydroxides in sulphurous acid decreases in the sequence cerium, didymium, lanthanum, thorium.

A. McK.

Chlorinated Antimonates. Metachloroantimonic Acid. RUDOLF F. WEINLAND and HANS SCHMID (*Zeit. anorg. Chem.*, 1905, 44, 37—64. Compare Weinland and Feige, *Abstr.*, 1903, ii, 218).—*Metachloroantimonic acid*, $\text{HSbCl}_6 \cdot 4\frac{1}{2}\text{H}_2\text{O}$, prepared by passing chlorine into a solution of antimony trioxide in concentrated hydrochloric acid until the solution becomes greenish-yellow and then passing hydrogen chloride into it, forms greenish-yellow, hygroscopic prisms. When its aqueous solution is kept, or when it is boiled, antimonic acid separates. Determinations of the lowering of the freezing point of aqueous solutions of metachloroantimonic acid indicated that two different ions were present. The authors were unable to obtain the compound, $\text{SbCl}_5 \cdot 5\text{HCl} \cdot 10\text{H}_2\text{O}$, described by Engel. The chlorine in metachloroantimonic acid is only partially precipitated by the addition of silver nitrate.

Ammonio-silver metachloroantimonate, $\text{AgSbCl}_6 \cdot 2\text{NH}_3$, forms golden-yellow, hexagonal plates, which gradually become white and finally violet. It is decomposed by water forming silver chloride and anti-

monic acid. *Ammonio-copper metachloroantimonate*, $\text{Cu}(\text{SbCl}_6)_2 \cdot 5\text{NH}_3$, forms blue, glistening prisms. The *cadmium* salt, $\text{Cd}(\text{SbCl}_6)_2 \cdot 7\text{NH}_3$, forms yellowish-white, dendritic crystals. The *zinc* salt, $\text{Zn}(\text{SbCl}_6)_2 \cdot 4\text{NH}_3$, forms white prisms. The *nickel* salt, $\text{Ni}(\text{SbCl}_6)_2 \cdot 6\text{NH}_3$, forms green, glistening prisms.

Pyridine silver metachloroantimonate, $\text{AgSbCl}_6 \cdot 2\text{C}_5\text{H}_5\text{N}$, forms golden-yellow crystals.

Pyridine copper metachloroantimonate, $\text{CuSbCl}_6 \cdot 5\text{C}_5\text{H}_5\text{N}$, forms prisms of an ultramarine-blue tint.

The *basic* salt, $\text{HSbCl}_6 \cdot 2\text{NH}_3$, formed by the addition of a large excess of ammonia to metachloroantimonic acid, crystallises in white, tetragonal pyramids.

The *pyridine* salt, $\text{HSbCl}_6 \cdot 2\text{C}_5\text{H}_5\text{N}$, forms microscopic needles. The *quinoline* salt, $\text{HSbCl}_6 \cdot 2\text{C}_9\text{H}_7\text{N}$, forms golden-yellow, silky, tetragonal plates.

Pyridine metachloroantimonate, $\text{HSbCl}_6 \cdot \text{C}_5\text{H}_5\text{N}$, forms colourless needles; it is stable and not hygroscopic. The *pyridine* salt, $\text{H}_3\text{Sb}_2\text{Cl}_{13} \cdot 3\text{C}_5\text{H}_5\text{N}$, forms colourless needles. *Quinolinemetachloroantimonate*, $\text{HSbCl}_6 \cdot \text{C}_9\text{H}_7\text{N}$, separates from alcohol in glistening, yellow needles. *Quinoline pyrochloroantimonate*, $\text{H}_2\text{SbCl}_7 \cdot 2\text{C}_9\text{H}_7\text{N} \cdot \text{H}_2\text{O}$, forms nacreous leaflets.

A. McK.

Alloys of Antimony and Bismuth. K. HÜTTNER and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, **44**, 131—144).—The curve of cooling of mixtures of antimony and bismuth has been studied by the authors. From molten masses rich in antimony, crystals rich in antimony first separate; the main amount of this molten mass solidifies about 50° below the temperature at which crystallisation begins. Molten masses which contain less than 70 per cent. of antimony do not crystallise until the melting point of bismuth is reached, and finally bismuth itself separates in almost a pure state. When alloys of antimony and bismuth are allowed to cool very slowly, the structure of the solid which separates is homogeneous; it is very probable that the two metals are miscible in all proportions. In molten masses containing antimony up to 60 per cent., the temperature at the beginning of the crystallisation remains constant for a time. The relationship between the temperatures at which crystallisation begins and the percentage of antimony is expressed by the tabulated results.

A. McK.

Inorganic Colloids. ALEXANDER GUTBIER and GUSTAV HOFMEIER (*Zeit. anorg. Chem.*, 1905, **44**, 225—228).—An unstable colloidal form of bismuth was obtained by the action of hypophosphorous acid on bismuth oxychloride. When a dilute solution of hydrazine hydrate is added to a hot dilute solution of ammoniacal copper sulphate, a copper hydrosol is obtained from which copper gradually separates. In the presence of gum arabic, this hydrosol is more stable. Attempts to prepare mercury hydrosol were unsuccessful.

A. McK.

Hexahydroxyplatonic Acid. ITALO BELLUCCI (*Zeit. anorg. Chem.*, 1905, **44**, 168—184).—A detailed account of work already published

(Abstr., 1904, ii, 180). In addition, the author has determined the electrical conductivity of the salt, $\text{Pt}(\text{OH})_6\text{K}_2$, which undergoes normal dissociation in dilute aqueous solutions and is regarded as a salt of a dibasic acid; it undergoes no hydrolysis at 25° and is analogous to potassium platinichloride. The transport numbers of its ions are calculated.

The crystalline form of the salt was measured.

A. McK.

Mineralogical Chemistry.

Souesite, a Native Iron-nickel Alloy from British Columbia. G. CHRISTIAN HOFFMANN (*Amer. J. Sci.*, 1905, [iv], 19, 319—320).—A grey, metallic sand forming the heavy residue from the gold washings on the Fraser River, near Lillooet, in British Columbia, consists of an iron-nickel alloy (47 per cent. of the whole sand) and scales of platinum (43 per cent.), together with flattened grains of iridosmine and gold, and grains of magnetite, ilmenite, quartz, and garnet. The iron-nickel alloy is in the form of small (the largest $1\frac{1}{2}$ mm. diameter), very irregularly-shaped, rounded grains of a faint yellowish-steel-grey colour, with sub-metallic lustre; it is strongly magnetic and is malleable. Analysis by F. G. Wait gave:

Ni.	Co.	Fe.	Cu.	Siliceous matter.	Total.	Sp. gr.
75.50	nil	22.02	1.20	1.16	99.88	8.215

This mineral, to which the name *souesite* is given, is thus very similar to the awaruite of New Zealand, the josephinite of Oregon, and to an iron-nickel alloy from Piedmont. L. J. S.

Synthesis of Naphtha and its Origin. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 79—83).—Since dextrorotatory naphtha derivatives have been obtained from several sources in the Caucasian district, and since the naphthene acids from kerosene are also optically active, the author considers that naphtha cannot be of exclusively inorganic origin. Optically active naphtha must be regarded as derived from plants or animals or both of these together, whilst inactive naphtha may be either inorganic or organic in its origin.

T. H. P.

Chrysoberyl from Canada. NEVIL NORTON EVANS (*Amer. J. Sci.*, 1905, [iv], 19, 316—318).—Chrysoberyl, a mineral not previously recorded from Canada, has been found with tourmaline in a pegmatite-vein traversing gneiss in Maskinonge Co., Quebec. The crystal examined is twinned and has the form of a hexagonal prism; it measures $1\frac{1}{2}$ inches across. Analysis gave:

GIO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	Total.	Sp. gr.
17.78	76.76	6.07	100.61	3.52

L. J. S.

Absence of Helium from Carnotite. E. P. ADAMS (*Amer. J. Sci.*, 1905, [iv], 19, 321—322).—The formation of helium from radium suggests that radioactive minerals should contain helium. The gases given off when pitchblende, monazite sand, and thorianite are heated exhibit the spectrum of helium, but the same result was not obtained with carnotite. Three hundred grams of carnotite, of activity 0·8 that of metallic uranium, were heated to redness in a vacuum for 3 hours; after absorbing carbon dioxide, 10 c.c. of gas remained, which, on removing nitrogen, was reduced to 0·1 c.c.; this small amount gave the characteristic red spectrum of argon. The absence of helium may be explained by the state of aggregation of the mineral, which forms a very fine powder disseminated through sandstone; this is extremely permeable to gases, whilst minerals known to contain helium are massive and impervious. L. J. S.

Physiological Chemistry.

Influence of Ozone on the Lungs. CHRISTIAN BOHR and VILH. MAAR (*Chem. Centr.*, 1905, i, 945; from *Skand. Arch. Physiol.*, 16, 41—66).—Ozone causes injury to the lung tissue, increases the oxygen intake and lessens the carbon dioxide output. W. D. H.

Output of Carbon Dioxide after the Administration of Various Sugars. JOHAN F. JOHANSSON, J. BILLSTRÖM, and C. HEIJL (*Chem. Centr.*, 1905, i, 944; from *Skand. Arch. Physiol.*, 16, 263—272).—Sucrose and lævulose have the same action on carbon dioxide excretion. Dextrose produces a greater output. Excretion of the gas and of sugar (in the urine) are not parallel. Sucrose is in the blood stream mainly an indifferent substance without influence on metabolism. The rapidity of combustion and of conversion into glycogen is less for lævulose than for dextrose. W. D. H.

Carbon Dioxide Production in Muscular Work. GUNNAR KORAEN (*Chem. Centr.*, 1905, i, 945; from *Skand. Arch. Physiol.*, 16, 381—389).—During hunger and great muscular work, the carbon dioxide in the blood is lessened, as well as during rest. This is not influenced by an exclusively fat diet, but the administration of sugar raises the amount to the normal level. In the first-named circumstances, the glycogen of the body is reduced to a minimum, and the decomposition of the body fat is increased by muscular work; but if the body has the opportunity to renew its store of glycogen, this substance participates in the process. W. D. H.

Physico-chemical Theory of Fertilisation. MARTIN H. FISCHER and WOLFGANG OSTWALD (*Pflüger's Archiv*, 1905, 103, 229—266).—The paper contains an account of colloidal solutions, including the

observations of Hardy, Bütschli, Quincke and others, and also of the methods by means of which such solutions (hydrosols) may be coagulated or transformed into hydrogels. A summary of the different methods of fertilisation is also given, including natural fertilisation by means of egg and spermatozoon, natural parthenogenesis, and artificial parthenogenesis, together with the different means by which the latter may be accomplished.

Fertilisation from the physiological point of view is regarded merely as the impetus to development of eggs, and from the morphological point of view consists in granulation, a phenomenon which is characteristic of all types of fertilisation.

All the artificial processes which can produce granulation of the ovule (fertilisation), for example, osmosis, specific action of salts, alteration of temperature, and mechanical methods, are the factors which can transform a hydrosol into a hydrogel, and the two processes are thus regarded as being similar if the egg-plasma is considered as a mixture of colloidal solutions.

The chief difference, morphologically, between natural fertilisation and ordinary coagulation is in the regular orientation according to which the granulation proceeds in fertilisation. This is attributed to the fact that in ordinary hydrogel formation granulation proceeds from numerous points, whereas in natural fertilisation it proceeds from one point only. In artificial parthenogenesis, granulation usually starts from several distinct points, and from this results the irregular nucleic and cell division often met with in such cases. J. J. S.

Ions and Cardiac Rhythm. STANLEY R. BENEDICT (*Amer. J. Physiol.*, 1905, 13, 192—204).—The experiments here recorded were performed with strips of tortoise heart muscle in various saline mixtures, and the results obtained do not bear out the views of Howell and other observers. The principal main conclusion drawn is that it is the anion, not the cation, which stimulates. W. D. H.

Alkalinity of Blood. ANASTAZY LANDAU (*Chem. Centr.*, 1905, i, 619—620; from *Arch. exp. Path. Pharm.*, 52, 271—288).—Blood was removed from the rabbit's carotid, coagulation prevented by sodium oxalate, and the alkalinity determined by the Zuntz-Loewy titration method. In another specimen, the proteids were first removed and the alkalinity (mineral alkalinity) then determined. The latter values agree well with Abderhalden's ash analyses. The total alkalinity of the plasma varies between 134 and 166 mg. sodium hydroxide per 100 c.c. The average value of the mineral alkalinity is 120.5, and of the proteid-alkalinity 25. The alkalinity of the red corpuscles is 852 (284 mineral, 568 proteid alkalinity). Poisoning by hydrochloric acid affects the proteid alkalinity most. Phosphorus poisoning has the same effect, but there are in this case other poisonous effects in addition to acid intoxication. W. D. H.

Blood-coagulation. VI. LEO LOEB (*Beitr. chem. Physiol. Path.*, 1905, 6, 260—286. Compare Abstr., 1904, ii, 496).—In the blood of the crab, two coagulations occur: the first, leading to the formation of "cell-

fibrin," is due to an agglutination of the corpuscles ; on filtering this off, the second coagulation of the plasma takes place. The second coagulation is much accelerated by the addition of muscle extract ; the power of muscle extract in this direction is weakened by heating it to 42°, and destroyed at 45°. Extract of cell fibrin acts similarly. The rate of coagulation of crab plasma is lessened by dilution with water, and still more so by dilution with sodium chloride solutions. There is also evidence of inhibitory substances in muscle extract. Calcium chloride has little or no influence on the formation of "cell fibrin," but it considerably hastens the coagulation of the plasma, produced by the addition of muscle and "cell fibrin" extracts. Potassium oxalate and to a less extent sodium fluoride hinder or prevent the coagulation of the plasma. Crab's fibrinogen was prepared by Halliburton's method, and the phenomena of coagulation observed in solutions of this are on the whole the same as in the intact plasma. In the majority of cases, a mixture of "cell fibrin" extract and muscle extract has a stronger coagulating action than either component. This opens up the question of "activating" substances, among which lecithin and serum must be reckoned. Leech extract has no inhibitory action on crab's blood.

In the blood of the king-crab (*Limulus*), it is not easy to distinguish the two coagulations, possibly because the second occurs so quickly.

The coagulation of the blood of vertebrates and invertebrates is very similar. In both, two substances are important, namely, the tissue *coagulins* and substances present in the blood itself. The coagulins are within certain limits specific. The substances in the blood itself are only specific in so far that those from vertebrate animals have no influence on invertebrate blood. It is probable that the materials extracted both from the cellular elements of the blood and from tissues like muscle act directly on the fibrinogen of the blood-plasma, but the conditions for their action are different, for instance, the acceleration by calcium salts is more marked with the coagulins than with the material from the blood-corpuscles. In certain circumstances, a combination of the two substances is more active than the sum of their individual activities ; that this is due to the influence of the coagulin in converting prothrombin into thrombin is only one of several possibilities.

W. D. H.

Laking of Red Corpuscles. Estimation of the Volume of the Blood-corpuscles. HANS KOEPPE (*Pflüger's Archiv*, 1905, 107, 183—186, 187—192).—All experiments hitherto have led to the conclusion that the red corpuscles become laked when their semi-permeable membrane is destroyed or injured. Laking is thus regarded as the criterion of the destruction of the corpuscle, and is therefore irreversible. But observations some years ago on blood mixed with solutions of ammonium salts and subjected to centrifugalisation showed that under certain conditions the layer of corpuscles beneath the colourless, supernatant fluid was laked, but on being poured out into a watch-glass and kept, the corpuscles were soon indistinguishable from normal ones, and had suffered no injury. The repetition of these experiments with a very perfect centrifuge, making 6000 turns per

minute, led to the discovery of the explanation. This centrifuge is so rapid in action that a separation of plasma and corpuscle can be accomplished before coagulation sets in, and mixture of the blood with foreign agents is unnecessary. After centrifugalising, the corpuscles are laked, but on standing subsequently their normal opaque appearance returns. The explanation is as follows: ordinary blood is opaque in the same way as an emulsion is, because of the different refraction of the corpuscles and the intervening fluid. The force of the centrifuge, however, is sufficient to press the corpuscles together, and they are placed wall to wall without any intervening fluid; the walls are composed of a fat-like material and are transparent, and so the whole mass of corpuscles is transparent. After the centrifugal force is stopped, and the blood is poured out into a watch glass, the usual condition of things is re-established. The invention of a centrifuge so perfect should render the determination of the volume of corpuscles by its means much more frequently employed than it is at present. The results have been regarded as doubtful in the past, different observers with different centrifuges obtaining inconstant figures. There need be no fear of an alteration in their volume, for, in order to press water through a semi-permeable uninjured membrane, a pressure of seven atmospheres is required, and such a pressure does not occur in the centrifuge.

W. D. H.

Union of Carbon Dioxide with Amphoteric Amino-substances. MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1905, 44, 85—96).—Amino-acids like asparagine, peptone, and the body proteids unite organically with carbon dioxide. The occurrence of such compounds in the blood and in muscle is a factor in respiratory exchange, and Bohr's compound of carbon dioxide with hæmoglobin thus appears in a new light. The same is true in vegetable physiology in reference to the question of carbon dioxide reduction.

W. D. H.

Behaviour of Sodium Fluoride towards Blood. MASATO TOYONAGA (*Bull. Coll. Agric. Tôkyô*, 1905, 6, 361—363).—Sodium fluoride (0.3 per cent.), like normal oxalates, checks coagulation. When larger amounts are employed (4 per cent. at 25° and 1 per cent. at the ordinary temperature), the serum becomes viscous, or almost gelatinous, due probably to its combining with the proteid of the blood. This would account for the stiffening of the muscles of a dead rabbit observed by von Fürth after injection of a 3 per cent. solution of sodium fluoride (*Abstr.*, 1903, ii, 440). This can, at any rate, have nothing to do with the lime present in the tissues, since it is now shown that injection of a 10 per cent. solution of potassium oxalate left the muscles of a dead rabbit soft and flexible even after 15 minutes.

Arthus (*Jahresb. Tierchem.*, 1901—1902) found that 0.3 per cent. of sodium fluoride had no effect on blood and that 0.5 per cent. gave a precipitate.

N. H. J. M.

Phosphorus Metabolism in Man. CARL TIGERSTEDT (*Chem. Centr.*, 1905, i, 946; from *Skand. Arch. Physiol.*, 16, 67—68).—On an almost phosphorus-free diet, the experimenter passed 0.134

gram of phosphorus in the fæces. How the phosphorus metabolism behaves with increase in supply of phosphorus is not decided. "Animal phosphorus" is, on the whole, better used than "vegetable phosphorus."
W. D. H.

Absorption and Excretion of Iron in the Alimentary Canal of Dogs and Cats. HUBERT SATTLER (*Chem. Centr.*, 1905, i, 621—622; from *Arch. exp. Path. Pharm.*, 52, 326—332).—By microchemical methods, it is shown that dogs and cats differ from herbivora in regard to the absorption and excretion of iron. Iron could not be demonstrated in the duodenal epithelium, and little or none in the lymph paths. In the large intestine, the results are also often negative. It is possible that iron is absorbed in a form not recognisable by the methods used.
W. D. H.

Behaviour of Various Polypeptides towards the Pancreas Ferment. EMIL FISCHER and EMIL ABDERHALDEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 290—300. Compare Abstr., 1903, i, 694, 800; 1904, i, 867, 890, 917; 1905, i, 121, 122).—The behaviour of a number of synthetical polypeptides towards the pancreas ferment at 36° has been investigated. The ferment solution was obtained by means of a Pawloff fistula, and rendered active by a 5 per cent. solution of intestinal fluid. The results are contained in the following table:

Hydrolysed.	Not hydrolysed.
Glycyl- <i>l</i> -tyrosine	Leucylproline
Leucyl- <i>l</i> -tyrosine	Glycylphenylalanine
Dialanyleystine	Glycylglycine
Dileucylcystine	Diglycylglycine
Alanyl-leucylglycine	Triglycylglycine
Tetraglycylglycine	
Ethyl triglycylglycine	

In the case of *r*-alanyl-leucylglycine, hydrolysis proceeds selectively, the products of change being *d*-alanine, optically active leucylglycine, and probably an optically active alanyl-leucylglycine. E. F. A.

Assimilation Limits of Sugars. FRANZ BLUMENTHAL (*Beitr. chem. Physiol. Path.*, 1905, 6, 329—341).—In both men and animals the assimilation limit for sugar is low; the ability of the organism to destroy sugar or store it as glycogen is thus limited, and the sugar appears in the urine. The majority of the experiments here recorded were performed by injecting different quantities of different sugars into rabbits and examining the urine. The limit for galactose is especially low; that for dextrose and lævulose is about equal. The numerical results are given in tables.
W. D. H.

Adenase. WALTER JONES and M. C. WINTERNITZ (*Zeit. physiol. Chem.*, 1905, 44, 1—10).—In the autolysis of organs, attention is drawn to three ferments concerned in the changes which occur in

purine derivatives. These are guanase, which converts guanine into xanthine, adenase, which converts adenine into hypoxanthine, and oxydase, which oxydises hypoxanthine into xanthine. These are independent of each other and are all present in thymus and suprarenal glands. In the pancreas, oxydase is absent or nearly so. In the spleen, guanase is almost entirely absent, adenase is present in abundance, and oxydase in small quantity. In the liver, the same is true except that oxydase is more abundant. These results are arrived at by examining the products of autolysis in each case, with and without the addition of one or other of the purine bases. W. D. H.

Proteolysis and Proteid Synthesis in the Animal Organism.

EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1905, 44, 17—52).—A discussion of the views of Kühne, Kutscher, and Fischer on the action of proteolytic ferments and on the question whether or not proteids are resynthesised in the body from simple cleavage products. Experiments on dogs are described in which the cleavage products were estimated in the contents of the alimentary canal and in which the urine was also examined. These are compared with the products of proteolysis obtained *in vitro* by Fischer's method. Some analyses of pathological urine are also given. The general conclusion drawn is that the breakdown of proteid into simple crystalline products is incomplete in the body. W. D. H.

The Importance of the Digestion of Proteids for their Assimilation. EMIL ABDERHALDEN (*Chem. Centr.*, 1905, i, 890—891; from *Centr. Stoffwechsel. u. Verdauungskrankh.*, 1904, 5, 649—651).—A paper on similar lines to the preceding one. W. D. H.

Glycogen. KARL GRUBE (*Pflüger's Archiv*, 1905, 107, 483—489, 490—496).—The glycogen in the liver is uniformly distributed; this is by no means an unimportant point when a small piece of liver only is analysed as a sample of the whole organ. This statement has been questioned in the past, but by Pflüger's method it is shown to be true. Any small variations are due to the relative admixture of connective tissue. By artificially perfusing the liver with defibrinated blood from the same animal (dog), to which various carbohydrates are added, it is shown that glycogen is formed from dextrose, dextrin, and lævulose, and the carbohydrate added to the blood becomes lessened. The liver should be kept *in situ*, and the artificial perfusion begun without any pause after the cessation of the natural circulation. The operative procedure by which this is done is described. W. D. H.

Twitchings of Skeletal Muscles produced by Salt Solutions. WALTER E. GARREY (*Amer. J. Physiol.*, 1905, 13, 186—191).—An examination of various salts in the production of twitchings in the skeletal muscles of frogs and mammals. In the latter animals, the contractions are feeble and not so rhythmic as in the frog.

W. D. H.

Influence of Alcohol, Sugar, and Tea on the Contractility of Muscle. A. F. HELLSTEN (*Chem. Centr.*, 1905, i, 945; from *Skand. Arch. Physiol.*, 16, 139—221).—The contractility of muscle is first increased by alcohol, and then diminished; it is increased by sugar and by tea. Practical considerations are pointed out. W. D. H.

Chemistry of Invertebrate Muscle. ARTHUR B. GRIFFITHS (*Chem. News*, 1905, 91, 146—147).—The muscles of various invertebrates were examined. They yielded myosin, musculin, myosinogen, myoglobulin, and myoalbumose. Analytical numbers obtained in each case are given for gases (CO_2 liberated at 60° , CO_2 liberated by acid, nitrogen), water, solids, coagulated albumins, soluble albumins, fat, gelatin, creatine, ash, and individual ash constituents. D. A. L.

Amount of Lime in Different Animal Organs. MASATO TOYONAGA (*Bul. Coll. Agr. Tōkyō*, 1905, 6, 357—360. Compare Abstr., 1904, ii, 751; and Aloy, *Jahresb. Tierchem.*, 32, 700).—The amounts of dry matter, ash, calcium, and magnesium dissolved from different livers by water, 1 per cent. acetic acid, and alcohol, and the amounts in the undissolved residues were determined. The results relating to calcium and magnesium are as follows: horse liver, Ca 0.1479, Mg 0.1681; bullock's liver, Ca 0.1918, Mg 0.1977; pig's liver, Ca 0.1779, Mg 0.1853 per thousand of fresh substance.

Human liver contains, according to Oidtmann, Ca 0.2842 and Mg 0.0125; whilst dog's liver (Aloy, *loc. cit.*) contains Ca 0.175—0.259 and Mg 0.048—0.066 per thousand. N. H. J. M.

Catalytic Decomposition of Hydrogen Peroxide. ARTHUR S. LOEVENHART (*Amer. J. Physiol.*, 1905, 13, 171—185. Compare Abstr., 1903, ii, 415).—Recent work by Cohnheim and others on co-ferments suggested the study of the effects of mixing various extracts on some well understood chemical process. The catalysis of hydrogen peroxide was selected for this purpose. Using the un-neutralised commercial material, it was found that the extract both of pancreas and muscle enormously accelerates its decomposition by liver extract, and this power is not destroyed by boiling. But it was further found that both boiled and fresh liver extract have the same influence on liver extract, and that when neutralised hydrogen peroxide is employed, no such acceleration occurs in any case; the accelerating action is simply due to the neutralisation of the retarding effect of the acid in the commercial preparation. It would therefore have been simple from the first experiments to have concluded that the pancreas and muscle contain a catalo-kinase or co-ferment. The whole kinase conception rests on equally flimsy foundations. W. D. H.

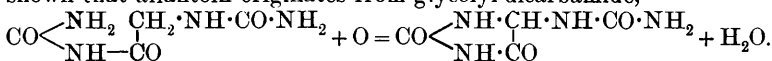
Uric Acid. RICHARD BURIAN (*Chem. Centr.*, 1905, i, 686; from *Med. Klinik*, i, 131—134).—A statement of the author's views on the origin of uric acid in man. An article on its destruction and excretion is to follow. W. D. H.

Formation of Allantoin in the Animal Body. HANS EPPINGER (*Beitr. chem. Physiol. Path.*, 1905, 6, 287—295).—*Hydantoamide*, $C_3H_7O_2N_3$, prepared by the action of aqueous ammonia on ethyl hydantoate, crystallises in rhombic prisms, melts at 180° , and is readily soluble in water, sparingly so in alcohol.

Glycolyldicarbamide, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2$, obtained by the interaction of molecular quantities of potassium cyanate, hydantoamide, and sulphuric acid, forms long prisms, melts at 158° , and is readily soluble in water, sparingly so in alcohol or ether.

In order to exclude the possibility that the reaction had taken the alternative course and so led to the formation of the isomeric *biuret-acetamide*, $NH_2 \cdot CO \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH_2$, this substance was synthesised by first treating ethyl hydantoate with potassium cyanate and sulphuric acid, when *ethyl biuret-acetate*, $C_6H_{11}O_4N_3$, was obtained, crystallising in thin, prismatic needles melting at 127° , and on treatment with ammonia yielding *biuret-acetamide*, which forms quadratic tablets and melts at 170° .

By feeding experiments on dogs and by perfusion of the liver, it is shown that allantoin originates from glycolyl-dicarbamide,



The formation of a closed ring by a vital oxidation process is interesting and may throw light on uric acid formation in birds. Oxidation of glycolyl-dicarbamide with calcium permanganate leads to a similar result.

W. D. H.

Lecithin in Heart and Kidneys in the Normal Condition, during Starvation, and in Fatty Degeneration. V. RUBOW (*Chem. Centr.*, 1905, i, 620; from *Arch. exp. Path. Pharm.*, 52, 173—204).—The lecithin of heart muscle constitutes 60—70 per cent. of the fatty extract after removal of all visible fatty tissue. This is much higher than in skeletal muscle. In inanition this alters but little, and in fatty degeneration produced by phosphorus or protracted chloroform poisoning the amount of lecithin may increase or remain normal. Experiments on the kidneys are incomplete; in the healthy state, the two kidneys contain an equal amount of lecithin.

W. D. H.

Anti-ferments. BEITZKE and CARL NEUBERG (*Chem. Centr.*, 1905, i, 943—944; from *Verh. d. deutsch. Pathol. Ges.*, 1905, 160—161).—Anti-emulsin was first prepared by rectal immunisation by Hildebrandt's method; it can also be obtained from rabbits after subcutaneous injections of emulsin. It is contained in the globulin fraction of the serum. Added to dextrose or galactose, after 8 days at 38° , there is an increase in optical activity, which thenceforth for $4\frac{1}{2}$ weeks remains unaltered. Lactosazone is then obtainable. Neither normal rabbit's serum nor that obtained after immunisation with emulsin leads in this way to disaccharide formation. The question as to whether other anti-substances have a synthetic function was investigated.

W. D. H.

The Catalase of Milk. EMIL REISS (*Chem. Centr.*, 1905, i, 684; from *Zeit. Klin. Med.*, 56, 1—12).—Cream decomposes hydrogen peroxide more vigorously than milk; this confirms Faitelowitz (*Diss. Heidelberg*, 1904). The catalase is associated with the fat globules in a physical way, and is insoluble in the presence of colloids.

W. D. H.

Human Bile. H. P. T. ØRUM (*Chem. Centr.*, 1905, i, 942—943; from *Skand. Arch. Physiol.*, 16, 273—333).—In addition to glycocholic acid, human bile contains a variable amount of glycocholeic acid.

W. D. H.

Perfusion Experiments on Excised Kidneys. TORALD SOLL-MANN (*Amer. J. Physiol.*, 1905, 13, 241—303).—A full account of experiments previously published (this vol., ii, 181).

W. D. H.

Effects of Ligature of One Ureter. MISS B. SHELDON AMOS (*J. Path. Bact.*, 1905, 10, 265—286).—Ligature of one ureter in rabbits and guinea-pigs leads after some weeks or months to death. This may be preceded by Cheyne-Stokes breathing and wasting, but only occasionally by slight albuminuria, and never by œdema. There are obvious changes in the affected kidney, and very slight ones in the other and in the liver; the heart is normal. Death cannot be due to the inability of one kidney to perform the work of the two, or to the internal secretion of one kidney being insufficient to sustain life, since extirpation of one kidney is not fatal. The poison is probably not due to absorption of the products of disintegration of the kidney cells, for these when injected are not toxic. Death is probably the result of absorption of the products of the secretion of the ligatured kidney.

W. D. H.

Precipitation of Lævulose from Urine by Lead Acetate. RUDOLF ADLER and OSCAR ADLER (*Ber.*, 1905, 38, 1164—1165).—Contrary to Külz's statement (*Zeit. Biol.*, 1890, 27, 235), lævulose is precipitated, often in considerable amount, from urine by the addition of lead acetate.

W. A. D.

Statistical Tables of the Amount of Nitrogenous Substances in Human Fæces. FELIX OEFELE (*Chem. Centr.*, 1905, i, 776—777; from *Ber. deut. pharm. Ges.*, 15, 17—29. Compare *Abstr.*, 1904, ii, 102).—The average percentages in dry substances are as follows: nitrogen in substances soluble in water, 2; in the ammonia group, 0·5; in the indole group, 0·8; in the urobilin group, 0·7; in the purine group, 0·1; in mucin, 0·2; in micro-organisms, 1·7; total nitrogen, 5·5. The proteid in the micro-organisms consists to a large extent of mucin.

W. D. H.

Composition of Blood and Exudations in Disease. KASIMIR VON RZENTKOWSKI (*Chem. Centr.*, 1905, i, 942; from *Virchow's Archiv*, 179, 405—450).—Hydræmia occurs in various acute and chronic infectious and anæmic conditions, in kidney disease, and in pneumonia.

Transudations are believed at first to be mere aqueous solutions of salts; the proteid in them is a secondary addition. Some details of total and residual nitrogen are also given. W. D. H.

Chemistry of Cancer. II. Abnormal Fermentative Occurrences. CARL NEUBERG (*Chem. Centr.*, 1905, i, 760; from *Berlin. Klin. Woch.*, 1905, 118—119).—The action of radium emanations on carcinomatous tissue is to influence the ferment action in the cancer cells. By autolysis of liver-cancer, a characteristic product appears, namely, free pentose; this is not formed from normal liver. This was confirmed in a case where the liver metastases originated from cancer of the stomach; the latter yielded no pentose. The high percentage of pentose in cancerous tissues is due to richness in nuclei. Normal liver juice does not influence the rate of autolysis in the lungs, but leads to the formation of albumoses (Jacoby, *Beitr. Chem. Physiol. Path.*, 3, 446); the juice of liver cancer leads to the opposite result, namely, an increase in simple cleavage products. W. D. H.

Blood Changes in Plague. LEONARD ROGERS (*J. Path. Bact.*, 1905, 10, 291—295).—In plague, the hæmoglobin and red corpuscles are not usually affected. Slight leucocytosis occurs during the first three days of the disease and usually disappears later. The leucocytosis mainly affects the lymphocytes. W. D. H.

Leucocytosis of Typhus Fever. ANDREW LOVE (*J. Path. Bact.*, 1905, 10, 296—327).—In typhus fever there is no evidence of destruction of red corpuscles; they may even be increased. This is evidence against Gotschlich's parasite being the cause of the disease. The leucocytosis resembles that in diplococcal infections. W. D. H.

Poisons applied to the Outer Surface of the Mammalian Heart. ALEXANDER BALDONI (*Chem. Centr.*, 1905, i, 621; from *Arch. exp. Path. Pharm.*, 52, 205—219).—The observations of Jacoby and Wybauw on the result of the application of helleborein to the outer surface of the frog's heart are here extended to mammals. Allylthiocarbimide and camphor have no important effect; physiological saline solution is wholly indifferent. A 0.9 per cent. solution of potassium chloride depresses the blood pressure, and stronger solutions stop the heart. Concentrated sodium chloride solution depresses blood-pressure also. Helleborein, digitalin, and bufotalin have the same effect and finally bring about diastatic stoppage of the heart. W. D. H.

The Urine in Phosphorus Poisoning. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1905, 44, 74—84).—In the urine in cases of phosphorus poisoning (rabbit and man), tyrosine, leucine, glycine, phenylalanine, alanine, and arginine are present. This is the first time a diamino-acid has been found in urine, but in a case of acute yellow atrophy of the liver Neuberg and Richter (*Deut. med. Woch.*, 1904, 30, 499) found lysine in the blood. W. D. H.

Antidote to Nicotine. C. ZALACKAS (*Compt. rend.*, 1905, 140, 741—742).—Experiments conducted on guinea-pigs and rabbits show that strychnine is not an effective antidote to nicotine poisoning; eserine is more effective, but the best antidote to nicotine is the alkaloid of *Nasturtium officinale*, two injections of the expressed juice of the plant completely counteracting the effect of a fatal dose of nicotine (0.025 gram) in the case of a rabbit, and similar results were obtained with dogs. M. A. W.

Influence of Radium Emanations on the Toxicity of Venoms. C. PHISALIX (*Compt. rend.*, 1905, 140, 600—602).—Exposure of the venom of the cobra and viper to radium emanations for 50 to 60 hours causes it to lose its toxic characters. The solution at the same time becomes opalescent owing to an agglutination of fine particles. The poison of the salamander or common toad is not affected. W. D. H.

Hirudin. ANDREAS BODONG (*Chem. Centr.*, 1905, i, 620—621; from *Arch. exp. Path. Pharm.*, 52, 242—261).—The substance named hirudin separated from leech extract has a very variable activity; the amount obtained diminishes on starvation; it is largest in amount in the autumn. The horse-leech forms none. Its power to inhibit fibrin formation is quantitative; excess remains free and active in the serum and passes into the urine in small amount. It produces no interference with circulation, respiration, or other bodily functions. W. D. H.

Action of Cresol in comparison with Phenol. KARL TOLLENS (*Chem. Centr.*, 1905, i, 622—623; from *Arch. exp. Path. Pharm.*, 52, 220—241).—The poisonous effects of phenol and of *o*-, *m*-, and *p*-cresols and their sodium compounds were investigated in frogs, mice, and cats. The differences noted are those of degree, *p*-cresol being decidedly more poisonous, *o*-cresol about equally poisonous, and *m*-cresol less poisonous, than phenol; the fatal doses exhibit a difference, but nothing very marked. The numbers obtained are given. W. D. H.

Action of Morphine and its Derivatives. ALEXANDER BABEL (*Chem. Centr.*, 1905, i, 623; from *Arch. exp. Path. Pharm.*, 52, 262—270).—Dionine, codeine, and heroine in comparison with morphine show pharmacodynamic differences. Mixed with brain substance, heroine is the one of which most is absorbed; heroine also is most soluble in fatty materials. Morphine is the least and dionine the most rapidly absorbed from the alimentary canal. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Metals on Fermenting Liquids. LEOPOLD NATHAN, ARTHUR SCHMID, and WILLY FUCHS (*Centr. Bakt. Par.*, 1905, ii, 14, 289—296. Compare Abstr., 1904, ii, 505).—Fruit musts, notwithstanding their greater acidity and consequently greater power of dissolving metals, are less injured than beer worts. Only gold, silver, and glass are quite indifferent. Copper and nickel are slightly injurious; iron, zinc, lead, brass, tin, and aluminium are very injurious.
N. H. J. M.

Origin of Fusel Oil. OSKAR EMMERLING (*Ber.*, 1905, 38, 953—956. Compare Abstr., 1904, ii, 834).—The fermentation of molasses by means of the organisms present on potato skins gives a mixture of ethyl, propyl, and *n*-butyl alcohols with lactic acid; amyl alcohol is not formed in this case. The principal organism causing the fermentation was isolated, but its nature is not yet definitely decided; contrary to the previous statement (*loc. cit.*), it is not strictly anaërobic. In presence of calcium carbonate, it ferments maltose, dextrose, and glycerol. With cane sugar, it gives rise to the foregoing alcohols, but the principal product is butyric acid with some acetic acid; carbon dioxide and hydrogen are evolved.
W. A. D.

Can Nitrite provide Oxygen in Anaërobic Culture of Bacteria? T. TAKAHASHI (*Bul. Coll. Agr. Tōkyō*, 1905, 6, 403).—The oxygen of nitrites cannot replace atmospheric oxygen in the case of *Bacillus pyocyaneus*, *B. subtilis*, *B. mesentericus vulg.* and *fuscus*, *B. acidilacti*, *Proteus mirabilis*, and the typhoid bacillus of mice.
N. H. J. M.

Chemical Changes attending the Aërobic Bacterial Fermentation of Simple Organic Substances. I. Carbamide, Asparagine, Albumose, and Rochelle Salt. WALTER E. ADENEY (*Proc. Roy. Irish Acad.*, 1905, 25, 6—24).—The author has studied the fermentation of carbamide, asparagine, albumose, and Rochelle salt by means of organisms which are not specified and which were present in the distilled water used or in other substances employed in making up the solutions. The fermentation in each case was conducted under aërobic conditions and the products were estimated at intervals.

The organisms capable of initiating and effecting the hydrolysis of carbamide appear to exert that change entirely by enzyme action. When the conditions of fermentation are such that carbamide is subject to the physiological process of respiration, that is, when carbamide is the sole nutrient organic substance present, it undergoes only partial hydrolysis, the greater portion of it being oxidised to carbon dioxide, nitrogen trioxide, and ammonia.

Asparagine, when fermented by water organisms under aërobic conditions, may undergo complete enzyme change into aspartic acid and ammonia during the earlier stages of the bacterial growth, and the aspartic acid subsequently undergoes respiratory changes. In the

case of albumose, the oxygen absorbed and the carbonic dioxide and ammonia formed were the result of respiratory changes. Rochelle salt is quickly fermented when mixed with carbamide. In the absence of any other source of nitrogen except atmospheric air, it ferments to a less extent; it is converted first into potassium sodium malate, carbon dioxide, and water, and then the malate is oxidised to carbon dioxide and water.

A. McK.

Action of Bacteria on Sugars. ADALBERT SEGIN (*Centr. Bakt. Par.*, 1904, ii, 12, 397—400).— α -Glucoheptose and quercitol were not attacked by any of the eight bacteria employed; both xylose and arabinose were decomposed by *Bacillus coli* and *B. enteris*.

The results accord with previous observations that aldehydic and ketonic sugars are much more readily attacked by bacteria than the corresponding alcohols.

N. H. J. M.

Bacteriological Examination of Tidal Mud. WILLIAM G. SAVAGE (*J. Hygiene*, 1905, 5, 146—174).—Mud samples yield more trustworthy bacteriological evidence of the degree of contamination of a tidal river than either water or oyster samples. The two latter only indicate immediate contamination; mud samples show evidence of part contamination for at least several weeks. Muds with high relative purity are safe for oysters. No evidence was obtained that either *Bacillus typhosus* or *B. coli* alter their characters in tidal mud. Typhoid bacilli readily survive for two weeks in tidal mud, and after that time their numbers as a rule rapidly decline.

W. D. H.

Relationship of the Pseudo-diphtheria and the Diphtheria Bacillus. G. F. PETRIE (*J. Hygiene*, 1905, 5, 134—145).—No substance capable of neutralising diphtheria antitoxin is present in filtrates of pseudo-diphtheria bacilli. Immunisation of horses with these filtrates does not produce an antitoxin to diphtheria toxin. The two bacilli, therefore, do not stand in any close relationship to each other.

W. D. H.

Modification of the Method for Isolating Nitrifying Micro-organisms. R. PEROTTI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 228—231).—This method is a modification of that given by Omeliansky (*Abstr.*, 1900, ii, 232) and makes use of blocks of ordinary commercial magnesium carbonate, which may be fashioned either as flat plates to fit into Petri dishes or as parallelipeds for employment in test-tubes. In the former case, the plate used is about 1 cm. in thickness, and the upper surface is rendered smooth by rubbing with a piece of unpolished glass and then with the fleshy part of the finger, whilst the under surface is hollowed out so as to allow more of the nutrient solution to be used. The latter consists of 50 c.c. of a solution containing 2 grams of ammonium sulphate, 1 gram of potassium phosphate, and 0.5 gram of magnesium sulphate per litre of water, this being mixed just before using with a drop of a 2 per cent. solution of ferrous sulphate and a drop of a saturated solution of sodium chloride. The parallelipeds are smoothed as above.

After the sterilisation of the magnesium carbonate and nutrient solution in the test-tube or Petri dish, the liquid containing the micro-organisms is poured over the surface of the block and the whole kept at 28—30° in a thermostat. After a time, the surface of the block exhibits small, regular excavations in which the magnesium carbonate has assumed a dirty-yellow coloration. Microscopic examination reveals the presence of numerous bacteria resembling Winogradsky's *Nitrosomonas europæa*.
T. H. P.

Influence of Different Carbohydrates and Organic Acids on the Decomposition of Nitrates by Bacteria. JULIUS STOKLASA and EUGEN VÍTEK (*Centr. Bakt. Par.*, 1905, ii, 14, 102—118 and 183—205).—The reduction of nitrates is due to the hydrogen, produced along with carbon dioxide, as the last products in the breaking down of carbohydrates and organic acids, and is similar to the reduction of arsenates, chlorates, and ferricyanides. Dextrose, lævulose, galactose, xylose, arabinose, and lactic, valeric, and succinic acids are all suitable as sources of carbon for the various bacteria which produce organic nitrogen from nitrates.

Xylan and araban and the corresponding pentoses are not very suitable for denitrification bacteria which liberate nitrogen, but seem to be available for the slow conversion of nitric and nitrous acids into ammonia. *Bacillus Hartlebi*, when cultivated in presence of arabinose, assimilated 33·62 per cent. of the total nitric nitrogen, converting it into proteids.

The widely distributed (in Bohemia) soil organism, *Clostridium gelatinosum*, together with *Bacillus mycoides*, *B. subtilis*, *B. mesentericus vulgatus*, &c., are of importance in the conversion of nitrates into ammonia (compare Laxa and Velich, *Ber. Versuchs-Stat. Rüben-zuckerind., k. k. böhm. techn. Hochschule in Prag*, 1902, 7). *Clostridium*, in arabinose, converted nearly 46 per cent. of nitric nitrogen into ammonia, whilst nearly 6 per cent. was utilised for proteid production.

N. H. J. M.

Fermentation-coefficient of Dead Yeast (Zymin) on Various Substrata. L. TELESNIN (*Centr. Bakt. Par.*, 1904, ii, 12, 205—216).—The coefficient, CO_2/O_2 , of zymin on sterilised water is higher than 1. Similar results were obtained with glycerol, mannitol, lactose, and ethyl alcohol. Quinine hydrochloride produced a decrease in the carbon dioxide and consequently a lower coefficient. Dextrose, fructose, maltose, and sucrose gave uniformly high coefficients which decreased after 48 hours; raffinose gave lower coefficients.

The disappearance of oxygen indicates the presence of an oxidising ferment (compare following abstract).

N. H. J. M.

Respiration and Fermentation of the Different Varieties of Dead Yeast. J. WARSCHAWSKY (*Centr. Bakt. Par.*, 1904, ii, 12, 400—407).—Zymase is produced in varieties of yeast which induce alcoholic fermentation (*Saccharomyces cerevisiæ* 1 Hansen, *S. Pombe*) and are cultivated on substrata capable of fermenting, but not when they are cultivated on non-fermenting substrata. In the case of *S. Pombe*,

however, no zymase was produced when ammonium phosphate was present.

S. Membranefaciens, which has no power of fermentation, does not contain zymase. The coefficients, which varied between 0.35 and 0.49, indicate the presence of an oxydase. N. H. J. M.

Is Germination Possible in Absence of Air? T. TAKAHASHI (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 439—442. Compare Abstr., 1903, ii, 170).—Former experiments with peas showed that germination did not take place in absence of air (compare Godlewski, Abstr., 1901, ii, 618, and 1904, ii, 507).

It is now shown that rice, which is accustomed to grow in swampy soils, will germinate in water alone, without addition of sugar and in absence of air. Alcohol was produced and there was a loss of 0.4354 gram of starch (in 2.3966 grams of seeds), which was consumed by intramolecular respiration after conversion into dextrose.

The normal respiration process is ascribed to the living protoplasm rather than to zymase (Godlewski), the amounts of which are generally very small (compare Mazé, Abstr., 1904, ii, 634, and Maximoff, *Ber. deut. bot. Ges.*, 1904, 22). N. H. J. M.

Processes of Assimilation. I. HANS EULER (*Chem. Centr.*, 1905, i, 941; from *Arkiv Kem. Min. Geol.*, 1, 329—345. Compare Abstr., 1904, ii, 761).—The pressed juice of *Boletus scaber* decomposes hydrogen peroxide with great vigour owing to the presence of an enzyme *Boletus catalase*. The action remains practically constant for several days and is increased by the addition of weak solutions of bases, but is inhibited by small quantities of weak acids. The enzyme thus resembles O. Löw's β -catalase and Senter's hæmase except that its action is more affected by the presence of acids. The decomposition of hydrogen peroxide by this catalase takes place within certain limits in strict conformity with the equation for reactions of the first order. According to an approximate calculation, the decomposing action of *Boletus catalase* on hydrogen peroxide is much greater than that of colloidal platinum. E. W. W.

Processes of Assimilation. II. Condensation Products of Formaldehyde. HANS EULER and ASTRID EULER (*Chem. Centr.*, 1905, i, 941; from *Arkiv Kem. Min. Geol.*, 1, 347—355. Compare Abstr., 1904, ii, 761).—The compound, $\text{CH}_2\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$, prepared by shaking a solution of *p*-aminobenzoic acid with a 40 per cent. solution of formaldehyde, loses $\frac{1}{2}\text{H}_2\text{O}$ at 85° and decomposes at 207° with evolution of gas; it is soluble in cold alkalis or acids, but insoluble in water. *Trimethyleneasparagine*, $\text{C}_7\text{H}_{10}\text{O}_4\text{N}_2$, obtained by saturating a 40 per cent. solution of formaldehyde with asparagine, swells up and decomposes at 203°; when dried at 85°, it becomes yellowish-brown. The actual molecular weight of this compound appears to be at least six times as great as that corresponding with the simplest formula. The stability of methyleneasparagine and other methylene-amines has been examined by the freezing point method. It was found that in 0.5 to 0.1 normal solutions no action takes place between formaldehyde

and glycollic acid, carbamide or asparagine, the corresponding methylene-amines being resolved into their components. Similar results have been obtained in the case of alanine and tyrosine. It may be assumed, therefore, that the formaldehyde formed by the assimilation of carbon dioxide by the green plant does not combine with amino-derivatives of this kind.
E. W. W.

Can Aluminium Salts enhance Plant Growth? Y. YAMANO (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 429—432).—Pot experiments with barley and flax in which ammonium alum (0.2, 1 and 2 grams per kilo. of soil) was compared with ammonium sulphate, to which monosodium sulphate was added to make the amounts of sulphuric acid correspond, showed that moderate amounts of aluminium have a stimulating effect on plant development. In water cultures, 0.2 per cent. of alum acted injuriously after 3 weeks, and 0.8 per cent. killed the plants in a few days.

G. Smith (*Chem. News*, 1903, 88, 135) found 36—43 per cent. and even 79.66 per cent. of alumina in the ash of the peripheral parts of *Orites excelsa*; and Radlkofer (*Ber. deut. bot. Ges.*, 1904, 22, 216) found in various kinds of *Symplocos* a colourless substance consisting chiefly of aluminum salts. These plants were named *Arbor aluminosus* by Rumphius in 1690.
N. H. J. M.

Production and Utilisation of Glycogen by Lower Vegetable Organisms. BERTHOLD HEINZE (*Centr. Bakt. Par.*, 1904, ii, 177—191, 355—371; 1905, ii, 9—21, 75—87, and 168—183. Compare Abstr., 1904, ii, 504).—Cultivations of *Aspergillus niger* utilised glycogen with production of sugar and acids, probably acetic and formic acids, but not oxalic acid. Similar results were obtained with other organisms. In the case of *Mucor*, however, no sugar could be detected among the products; probably it is at once converted into alcohol and acids.

Attention is called to the importance of glycogen in connection with yeast fermentation and in the processes of assimilation of free nitrogen by azotobacter and by leguminous bacteria.

In experiments with nitrogen-assimilating organisms, it was found that satisfactory results could only be obtained with certainty when considerable amounts of soil were employed (1—10 grams per 100 c.c.). Pectin substances may be used with advantage in cultivations of azotobacter, and potassium phosphate is very beneficial.

N. H. J. M.

Flowering of Bamboo. OSCAR LOEW (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 365—369).—A barley plant grown in water-cultures was transferred when 29 cm. high to a fresh solution containing much more calcium nitrate and very much less magnesium sulphate. The change in the composition of the solution resulted in a very marked increase in the size of the leaves, but did not accelerate leaf formation. The plant died early owing, perhaps, to the precipitation of the soluble phosphates of the protoplasm as calcium phosphate.

Prolonged experiments with bamboo itself will be necessary to

ascertain the best means of checking the formation of buds. The results of observations made with annual grasses indicate that large applications of gypsum and sodium nitrate in conjunction with irrigation may be of use.

It is suggested that an application of dipotassium phosphate might prolong the lives of the leaves of the flowering *Gramineæ*, since it is probably this salt which is chiefly withdrawn from the leaves for seed production. Wolff and Ritthausen state that one rôle of silica is to hasten the death of the leaves in favour of the seed (compare also Kreuzhage and Wolff, *Abstr.*, 1884, 1211). N. H. J. M.

Source and Composition of the Essential Oil of Herb Bennett Root: A New Glucoside and Enzyme. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1905, 140, 870—872).—The dried root of Herb Bennett (*Geum urbanum*) has a feeble odour resembling that of cloves. If the plant be carefully plucked so as to leave the root intact, there is no manifestation of the characteristic odour, but this is at once detectable when the root is crushed between the fingers. The explanation of this phenomenon was established by the following experiments.

By extraction of the fresh root with boiling alcohol of 95°, distillation of the extract under reduced pressure, extraction of the residue with alcohol, and precipitation of the solution by excess of ether, a substance is obtained which is odourless, but, however, contains the substance which gives rise to the odoriferous principle. This proves to be eugenol.

Another portion of the root was macerated with sand and extracted with cold alcohol of 90°. The residual powder, which contains an enzyme, was dried at 30°. On adding to an aqueous solution of the first substance a little of the ferment powder, a distinct odour of cloves is at once evident. If the ferment powder is previously heated in boiling water, the effect is not observable. It is concluded from these observations that the odoriferous principle does not exist free in the Herb Bennett root, but is produced from some other substance present by the action of an enzyme. The substance is a glucoside; on addition of the enzyme to its aqueous solution, the reducing power and the rotary power both gradually increase.

The active enzyme is characteristic; the resolution of the glucoside is not effected by emulsin, invertase, nor by the enzyme of *Aspergillus niger*. It cannot be extracted by treatment of the roots with water.

The glucoside can be isolated in globular crystals by addition of ether to the alcoholic solution. The term *gêin* is proposed for the glucoside, and *gêase* for the enzyme. H. M. D.

Fertilising Principles required by the Tobacco Plant. CHARLES GIRARD and E. ROUSSEAU (*Compt. rend.*, 1905, 140, 733—735).—The authors have determined the impoverishment effected in the soil by the growth of the tobacco plant by estimating the quantity of nitrogen, phosphoric acid, potassium and calcium in the leaves, stems, roots, cuttings, and prunings of the plant. The results are tabulated in the original, and show that the efficiency of the

tobacco plant regarded as a vegetable machine is very low, only about one-half of the energy of the plant being expended in the production of the marketable product, namely, the leaves; on the other hand, the waste products form valuable manures. M. A. W.

Further Observations on Oxydases. KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 371—374).—Guaiacol is less sensitive towards peroxides than potassium iodide-starch, and its reaction with nitrites much weaker than the iodine reaction. The loss of the power of liberating iodine which certain plant juices undergo when heated is attributed to the acidity of the juice and the presence of traces of amino-compounds, which together bring about the destruction of nitrites.

The substance which gives the guaiacol reaction is not the same as the one which liberates iodine (compare Bach and Chodalt, *Abstr.*, 1904, i, 359). N. H. J. M.

Ammoniacal Nitrogen as Plant Food. MAX GERLACH and IGNAZ VOGEL (*Centr. Bakt. Par.*, 1905, ii, 14, 124—128. Compare Mazé, *Abstr.*, 1900, ii, 499).—Experiments in which maize was grown in sterilised soil (5.5 kilos.) without nitrogenous manure and with nitrogen (0.5 gram) in the form of ammonia and nitrate respectively showed that practically the whole of the ammoniacal nitrogen was assimilated, the production of dry matter being considerably increased.

Both manures, especially ammonium sulphate, retarded the growth at the commencement. The final increase in dry matter above ground was 31 per cent. with ammonium sulphate and 46 per cent. with nitrate (compare Takabayashi, *Abstr.*, 1897, ii, 585). N. H. J. M.

Comparison of the Organic Matter in Different Soil Types.

FRANK K. CAMERON (*J. Amer. Chem. Soc.*, 1905, 17, 256—258. Compare *Abstr.*, 1904, ii, 286).—Analyses of a large number of soils and subsoils shows that the average amounts of organic matter are respectively 2.06 and 0.83 per cent. In individual cases, the subsoil contains more organic matter than the surface soil. As a rule the colour of a soil varies with the amount of organic matter present, provided that the soils examined belong to the same type; but soils of different types cannot be compared in this manner owing to differences in colour due to mineral constituents and to differences in the character of the organic matter itself. The variations in the amounts of organic matter in the soils of one type are as great as between soils of different types. N. H. J. M.

Influence of Sodium Salts in the Soil on the Composition of Sugar Cane. H. C. PRINSEN-GEERLIGS (*Chem. Centr.*, 1905, i, 897; from *Med. Proefstat. Suikerriet West Java*, No. 76).—Most of the chlorine in sugar cane is in combination with potassium, very little sodium being present. Sodium salts cannot take the place of potassium salts in sugar cane, and plants manured with sodium chloride soon fail if there is a deficiency of potassium in the soil.

N. H. J. M.

Different Degrees of Availability of Plant Nutrients. OSCAR LOEW and KEIJIRŌ ASŌ (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 336—346).—The ratios CaO/MgO which were found to be 1, 2 or 3, and 4 for cereals, for more leafy crops, and for tobacco respectively, are only correct when the two substances are present in the soil in equally available forms, as, for instance, when they are both present as carbonates. When calcium is present as carbonate and magnesium as sulphate, the ratio is 30:1 for rice in sand-cultures, and 7:1 in a soil containing much calcium zeolites and a little magnesium sulphate.

Experiments with barley manured with calcium carbonate (5 per cent.) and with gypsum (5 and 20 per cent.) in addition to double superphosphate, potassium sulphate, and ammonium nitrate showed that calcium carbonate increased the percentage of calcium in the plant ash much more than the larger amount of calcium sulphate. This is attributed to the low degree of availability of gypsum, the solubility of which is not increased by dilute acids.

Lower yields after liming certain soils are not always due to diminished solubility of phosphoric acid, but may sometimes be the result of an unfavourable lime-magnesia ratio. N. H. J. M.

Injurious Effect of an Excess of Lime applied to the Soil. S. SUZUKI (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 347—351).—Pot experiments with rice grown in soil showed that an excess of calcium carbonate greatly reduced the yield, even when the phosphoric acid was applied in the form of disodium phosphate. An equivalent amount of calcium sulphate greatly increased not only the total yield, but especially the amount of grain. Liming did not, therefore, diminish the availability of the phosphoric acid, but its assimilability in the cells themselves. The difference in the action of the two calcium salts is due to the low solubility of calcium sulphate and the greater solubility of the carbonate due to root acidity. Moderate amounts of calcium carbonate had no injurious effect, owing to the presence of 11 per cent. of humus in the soil.

Powdered magnesite added in such quantity that the ratio CaO/MgO was 1:3 greatly reduced the yield.

When bone-dust and disodium phosphate were applied alone, the production of seed was practically the same. N. H. J. M.

Is the Availability of Phosphoric Acid in Bone-dust Modified by the presence of Gypsum? TOMIO KATAYAMA (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 353—356).—Sand culture experiments are described in which rice received, in addition to bone-dust, nitrogen and potash, calcium and magnesium carbonates in different proportions, and calcium sulphate with different amounts of magnesium carbonate. The gypsum plants grew much better than those which received carbonate, and had a much better colour. An excess of magnesia was unfavourable.

Results of experiments in which the phosphoric acid was applied as dicalcium phosphate also showed that an excess of lime over magnesia has no injurious effect when present as gypsum.

The depression in the availability of bone-dust by moderate amounts of calcium carbonates is not opposed to Suzuki's results (preceding abstract), being due to the absence of humus. N. H. J. M.

Influence of Various Ratios of Phosphoric Acid to Nitrogen on the Growth of Barley. RANA BAHADUR (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 421—428).—Barley was grown in pots containing 8 kilos. of soil to which 5 grams of double superphosphate and 1·995, 5·985, 11·970, and 17·955 grams of ammonium nitrate were added. The ratios $P_2O_5:N$ were, therefore, 3:1, 3, 6, and 9 respectively.

The greatest numbers of stems and ears and the greatest weights of ears and grain were obtained when the ratio $P_2O_5:N$ was 3:3; the greatest weight of straw when the ratio was 3:6. The lowest results, both grain and straw, were with the ratio 3:9. An analysis of the grain of the best plants (No. 2) showed that the ratio $N:P_2O_5$ was 100:37·3 (compare Stahl-Schröder, *J. Landw.*, 52, 80).

Further experiments were made in which a constant amount of ammonium nitrate (18 grams) was applied along with varying amounts of double superphosphate (5, 7·3, and 10 grams). The results of the experiment (which had to be discontinued before the flowering period) showed that the ratio $P_2O_5:N=1:3$ was less favourable than the ratio 1:2 and that the considerable amount of ammonium nitrate applied was not injurious. N. H. J. M.

Manuring with Kainite. S. SUZUKI (*Bull. Coll. Agr. Tōkyō*, 1905, 6, 505—519).—Pot experiments with peas, buckwheat, rice, and beans showed that the application of kainite was favourable in every case. The conclusion is drawn that kainite can only act injuriously when the soil contains excessive amounts of chlorides or magnesium. N. H. J. M.

Analyses of some Animal Excrements. JOHN MCCRAE (*Chem. Zeit.*, 1905, 29, 364).—Analyses of some guano-like deposits found in the Transvaal and possessed of more or less manurial value. L. DE K.

Analytical Chemistry.

An Improved Gas Apparatus. J. E. BABB (*J. Amer. Chem. Soc.*, 1905, 27, 156—158).—A modification of the Orsat apparatus, fully illustrated.

The apparatus has been constructed with a view to making a larger number of determinations. Its principal feature is an arrangement for bubbling the gases through the solutions.

L. DE K.

New Automatic Pipettes. GREINER and FRIEDRICHs (*Zeit. angew. Chem.*, 1905, 18, 465).—A modification of the authors' well-known automatic pipette, enabling the overflow liquid to be returned readily to the pipette.

A doubly-acting pipette is also described, the tap of which is so constructed that one pipette is filled as the other is emptied.

L. DE K.

New Burette for Volumetric Analyses. W. N. IWANOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 91—92).—This apparatus consists virtually of two burettes fixed side by side and having a common tap with two borings at right angles to one another, one for each burette, and also two separate nozzles. Two liquids may thus be titrated without removing the titration vessel from under the burette, so that time is saved. Besides this, the new arrangement only requires one stand and is hence more stable and occupies less space than two separate burettes and is cheaper to construct than the latter.

T. H. P.

Crucible Refrigerator. RUDOLF L. STEINLEN (*Chem. Zeit.*, 1905, 29, 364—365).—When heating a mixture of a silicate with calcium carbonate and ammonium chloride over a blast (Lawrence Smith's method), in order to prevent volatilisation of alkali chlorides it is important that the lid shall not get overheated. For this purpose the author uses a small bottle-shaped vessel through which a current of water flows; this is suspended at half a mm. distance from the lid.

L. DE K.

A New Filter. PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1905, 27, 287—292).—A convenient amount of Swedish filter-paper is crushed into a ball and placed in a ceresin-coated vessel and covered with hydrochloric acid of sp. gr. 1.12—1.18. A little hydrofluoric acid is added and the whole is stirred with a paraffin-coated wooden stirrer until the paper has turned into a mass of fine soft pulp, when distilled water is added. When a filter is required, some of this pulp is poured into a filter-tube of ordinary shape in the bottom of which is a rubber stopper fitted with a glass tube for attachment to the suction flask. On the stopper, when inserted into the tube, is a disc of piano-felt, 3/10 inch thick, fitting closely into the tube. The filter, if found to be of the desired thickness, is washed a few times with water and is then ready for use. When dealing with precipitates of barium sulphate and the like, the filter should be well compacted by hard stamping.

L. DE K.

Estimation of Water in Foods and Physiological Preparations. FRANCIS G. BENEDICT and CHARLOTTE R. MANNING (*Amer. J. Physiol.*, 1905, 13, 309—329).—The errors entering into the determination of water by the usual methods are: (1) volatilisation of material other than water, (2) absorption of oxygen, and (3) abstraction of moisture from the air during the process of weighing. A description of various matters of technique to obviate

these errors is given; for instance, the use of vacuum desiccators and of a low temperature to minimise the loss first mentioned.

W. D. H.

Estimation of the Halogens in Mercury Compounds. THEOPHILE FISCHER (*Chem. Zeit.*, 1905, 29, 361—362).—About 0.5 gram of the bromide or chloride is heated in a Bunsen flask with 5 c.c. of 10 per cent. sodium hydroxide for 20 minutes. When cold, 3 c.c. of dilute sulphuric acid (1:1) is gradually added, and, after cooling, 0.4 gram of potassium permanganate suspended in 10 c.c. of dilute sulphuric acid. Without delay, the flask is connected with a suitable condensing arrangement and the halogen is boiled off and collected in a solution of potassium iodide. The liberated iodine is then titrated as usual.

The iodine contained in mercuric iodide may be conveniently estimated by treating the compound with magnesium powder in the presence of 10—20 c.c. of water. The filtrate contains magnesium iodide which is then precipitated with silver nitrate, &c. L. DE K.

Estimation of Chlorine in Urine. WILLIAM M. DEHN (*Zeit. physiol. Chem.*, 1905, 44, 11—16).—A modification of Volhard's method is recommended as rapid, accurate, and specially suitable for clinical work. A small quantity of sodium peroxide is added to 10 c.c. of urine, and the mixture evaporated on the water-bath; 10 c.c. of water and dilute nitric acid are successively added, until the reaction is distinctly acid. A little ferric nitrate is added as indicator, and then titration with potassium thiocyanate and silver nitrate is performed. The operation can be completed in two minutes.

W. D. H.

Alkalimetric Estimation of Iodine. GIUSEPPE BARBIERI (*Chem. Centr.*, 1905, i, 693; from *Boll. Chim. Farm.*, 44, 6—7).—Thirty c.c. of *N*/10 soda are mixed with 30—40 c.c. of a perfectly pure and neutral 1 per cent. hydrogen peroxide solution and 25 c.c. of the iodine solution to be tested. The colourless liquid is then heated for some minutes at 100° in order to decompose the excess of peroxide and the liquid titrated with *N*/10 sulphuric acid, using methyl-orange as indicator. The amount of alkali which has entered into combination with the iodine, multiplied by 3.1665, gives the free iodine in the 25 c.c. taken.

L. DE K.

Estimation of Sulphur in Burnt Pyrites. K. JENE (*Chem. Zeit.*, 1905, 29, 362).—The usual method still practised in many works is the wet process including precipitation with barium chloride without previous elimination of the iron.

The author states that a large proportion of the sulphur is retained in the insoluble residue and advocates the fusion with the oxidising mixture recommended by Fresenius, or treatment with sodium peroxide.

L. DE K.

Estimation of Combined Sulphuric Acid by the Processes of Lunge and of Silberberger. GEORG LUNGE (*Zeit. angew. Chem.*, 1905, 18, 449—460).—As the result of an analysis of a sample of iron

pyrites by twelve different analysts in various parts of Europe, it has been shown that the process devised by Lunge gives correct results in the assay of pyrites, and that Silberberger's strontium process should not be used. The following details should be attended to: the solution should be mixed with an excess of 5 c.c. of ammonia; after warming at 70° for 10–15 minutes, the ferric hydroxide is collected and washed with boiling water until the filtrate measures 500 c.c. After acidifying this with hydrochloric acid and then adding 1 c.c. in excess, the liquid is precipitated with barium chloride, as usual. L. DE K.

Estimation of Sulphuric Acid by means of Benzidine Hydrochloride, and the Estimation of Sulphur in Pyrites. GEORG VON KNORRE (*Chem. Centr.*, 1905, i, 628; from *Chem. Ind.*, 28, 2–13).—The benzidine method gives good results in the presence of ferrous, copper, cobalt, zinc, nickel, manganese, and aluminium compounds. Ferric salts, particularly ferric chloride, seem prejudicial, owing to oxidation of the benzidine. Reduction of the ferric compounds may be effected by means of hydrazine or hydrogen sulphide, and, when sufficient ammonium hydroxide is added to form a small permanent precipitate, by means of hydroxylamine hydrochloride. In the estimation of sulphur in pyrites, the addition of a small quantity of hydroxylamine hydrochloride to the benzidine solution eliminates the errors due to ferric iron. An excess of ammonium nitrate must be avoided. G. D. L.

Oxidation of Sulphites by Iodine in Alkaline Solution. R. HARMAN ASHLEY (*Amer. J. Sci.*, 1905, [iv], 19, 237–239).—Rupp has recently proposed to titrate sulphurous acid with iodine solution in the presence of sodium hydrogen carbonate. It is necessary to add an excess of iodine, which is then, in turn, titrated with sodium thiosulphate.

The author shows that the process gives results approximating to the truth, but that this is merely due to a balancing of errors. If the excess of iodine is titrated by means of arsenious acid, it will be found that the sulphite has been but incompletely oxidised. On the other hand, when titrating iodine with thiosulphate in an alkaline instead of an acid solution, less iodine will be found than is really present, and consequently the amount of iodine consumed by the sulphur dioxide will appear greater than it really is. L. DE K.

Estimation of Ammonia in Milk. W. N. BERG and HENRY C. SHERMAN (*J. Amer. Chem. Soc.*, 1905, 27, 124–136).—A slight modification of the Boussingault-Schaffer method originally devised for the estimation of ammonia in urine.

Fifty c.c. of the sample of milk are introduced into a 2-litre flask and, after adding 50 c.c. of methyl alcohol, mixed with 10 grams of salt and 0.5 gram of sodium carbonate. Should the milk be very acid, a suitable additional amount of alkali should be added. After connecting with the suction pump, the mixture is heated at 60–65°, and from 30–60 c.c. (usually between 45 and 55 c.c.) are distilled and collected in two receivers containing together 25 c.c. of *N*/20 sulphuric acid diluted with water to 40 c.c. The excess of

acid is then titrated by means of *N*/20 sodium hydroxide, using congo-red as indicator. As the presence of methyl alcohol affects the titration, the liquid should be measured before the final titration; the volume, less 40 c.c., gives the amount actually distilled over. The corresponding correction to be applied is 0.5 c.c. alkali for 30–39 c.c., 0.6 c.c. for 50–60 c.c. of distillate. Using this process, the distillate is practically free from albuminoid or cleavage ammonia.

There seems to be no fixed relation between the ammonia and the acidity.
L. DE K.

Volumetric Method of Estimating Hydroxylamine. LOUIS J. SIMON (*Compt. rend.*, 1905, 140, 724–727).—Hydroxylamine salts cannot generally be titrated directly with potassium permanganate, owing to the varying reducing effects of the acid with which the hydroxylamine is combined; if, however, an equivalent quantity of sodium oxalate is added to a solution of the hydrochloride, sulphate, or nitrate of hydroxylamine, the mixture behaves as if it were pure hydroxylamine oxalate and can be titrated exactly with potassium permanganate (compare Abstr., 1903, ii, 239). The result is not affected by the addition of excess of sodium oxalate, whilst a mixture of hydroxylamine nitrate and less than the equivalent quantity of sodium oxalate behaves like a mixture of the oxalate and nitrate of hydroxylamine, each independently reducing the permanganate. Slightly abnormal results are obtained (i) when the quantity of sodium oxalate in excess of the theoretical is very small; this is due to the action of the dilute solution of sodium oxalate on the reducing power of the hydroxylamine oxalate; (ii) when the total quantity of sodium oxalate added is small; this is due to the action of the hydrogen potassium oxalate on the reducing power of the hydroxylamine oxalate.
M. A. W.

[Colorimetric] Estimation of Nitrogen as Nitrites in Waters. ROBERT SPURR WESTON (*J. Amer. Chem. Soc.*, 1905, 27, 281–287).—The author approves of Ilosvay's modification of the Griess-Warrington method, in which the reagents are dissolved in acetic instead of hydrochloric acid. He thinks, however, that the process may still be further improved by making the solutions more concentrated, and suggests the following proportions: 8 grams of sulphanilic acid in 1 litre of acetic acid of sp. gr. 1.044 and 8 grams of α -naphthylamine in 1 litre of acetic acid. Two c.c. of each of these reagents are to be added to 100 c.c. of the sample to be tested.
L. DE K.

Diphenylamine as Reagent for Nitrites, Nitrates, Chlorates, and its use when mixed with Resorcinol and β -Naphthol. EUGENIO P. ALVAREZ (*Chem. News*, 1905, 91, 155).—The colorations observed with diphenylamine are noted, but when 5 or 6 drops of a solution containing a decigram each of diphenylamine and resorcinol dissolved in 10 c.c. of sulphuric acid are poured on a milligram of nitrate, the liquid turns a yellowish-green with blue edges, becoming orange when alcohol is added. Nitrites give a deep bluish-violet with red margin, becoming red with alcohol. With chlorates, this mixture

is not satisfactory; when, however, the resorcinol is replaced by an equal weight of β -naphthol, a dull green coloration is obtained, which changes to grey or black when kept or when alcohol is added to it.

D. A. L.

Estimation of Phosphorus in Phosphor-bronze. DINAN (*Chem. Centr.*, 1905, i, 769; from *Mon. Sci.*, [iv], 19, 94).—Three to five grams of the alloy are dissolved in dilute nitric acid (1 : 1), and the insoluble tin oxide which retains the phosphoric acid is boiled with a solution of 7 grams of oxalic acid and 7 grams of ammonium oxalate until completely dissolved. The tin is deposited by electrolysis and in the liquid the phosphorus is estimated by the molybdate process, or, if preferred, by precipitation with magnesium citrate solution.

L. DE K.

Colorimetric Estimation of Phosphorus [in Iron]. THOMAS E. HEWITT (*J. Amer. Chem. Soc.*, 1905, 27, 121—124).—The phosphomolybdate precipitate, obtained in the usual manner from 2 grams of pig-iron or steel, is washed with a 2 per cent. nitric acid and then dissolved in the smallest quantity of *N*/10 sodium hydroxide. A further quantity of soda, one-half of that already used, is added, and the whole diluted to 100 c.c. An aliquot part is introduced into a 50 c.c. Nesslerising tube, and after passing a current of hydrogen sulphide for 5 minutes the tube is put into boiling water for another five minutes. After cooling and diluting to the mark, the colour is, as usual, compared with a standard solution treated with hydrogen sulphide in the same manner. This standard solution is made by dissolving 0.2737 gram of yellow precipitate in alkali, as directed, and diluting to 500 c.c.; 10 c.c. = 0.009122 mg. of phosphorus.

L. DE K.

Estimation of Phosphoric Acid by the Method of Ignition with Magnesium Nitrate and by that of Digestion with Acids. BURT L. HARTWELL, A. W. BOSWORTH, and J. W. KELLOGG (*J. Amer. Chem. Soc.*, 1905, 27, 240—244).—Before the molybdate process is applied, any organic matter should be completely destroyed, and this is effectually done by ignition with magnesium nitrate or in the wet way by heating in a Kjeldahl flask with sulphuric and nitric acids. The authors think that the most accurate estimations can be made by the ignition method, as the magnesium pyrophosphate obtained finally in the acid process is somewhat impure; this may, however, be partly remedied by redissolving the precipitate in nitric acid and reprecipitating with ammonia.

L. DE K.

Estimation of Phosphoric Acid in Food-stuffs. HENRI PELLET (*Ann. Chim. anal.*, 1905, 10, 93—95).—A reply to the criticism of Fleurent (*ibid.*, 12, 1904).

L. DE K.

Detection of Arsenic by means of the Marsh Apparatus. GEORG LOCKEMANN (*Zeit. angew. Chem.*, 1905, 18, 416—429).—An historical review of the various forms of the Marsh apparatus and

of the treatment of the substance to be examined therein. An illustration is given of an improved form as used by the author.

The best results are obtained with zinc which has been dipped for a minute in a 0.5 per cent. solution of pure copper sulphate and then washed. The author recommends drying the hydrogen evolved over *crystallised* calcium chloride.

L. DE K.

Estimation of Arsenic in Fuels. GEORGE MCGOWAN and R. B. FLORIS (*J. Soc. Chem. Ind.*, 1905, 24, 265—266).—The sample is ignited with lime to obtain the total arsenic and without lime to determine the non-volatile arsenic. The residues are dissolved in dilute hydrochloric acid, the arsenic is reduced by the addition of sulphurous acid and precipitated with hydrogen sulphide. The arsenic trisulphide is then collected on an asbestos filter and subsequently boiled out with water according to the method first described by F. Platten, who found that when arsenic trisulphide is boiled with water it is converted quantitatively into oxide, which remains in solution. The aqueous solution obtained is examined in a Marsh apparatus.

W. P. S.

Interference of Mercuric Chloride with the Formation of Arsenic, Antimony, and Phosphorus Hydrides. DIOSCORIDE VITALI (*Chem. Centr.*, 1905, i, 769; from *Boll. Chim. Farm.*, 44, 49—55).—Attention is called to the fact that owing to the formation of an arsenical mercury compound the presence of mercury, particularly in the form of mercuric chloride, may seriously interfere with the formation of arsenic hydride in the Marsh apparatus, most probably owing to the formation of Franceschi's compound, $\text{AsHg}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$. The reaction may conversely be utilised for the detection of traces of mercuric chloride with which, on addition of zinc, hydrochloric acid, and arsenious acid, a yellow to brown coloration or a brown precipitate is obtained. The formation of antimony hydride or phosphorus hydride is also interfered with by the presence of mercury chloride.

L. DE K.

Destruction of Organic Matters in Toxicological Investigations. A. GRIGORÉEFF (*Chem. Centr.*, 1905, i, 771—772; from *Viertelsschr. ger. Med. öffent. Sanitätswesen*, 29, 74—78).—Ten grams (or more) of the dried substance are heated with 10 times the bulk of sulphuric acid until dissolved. It is then again heated with occasional addition of 10 c.c. of fuming nitric acid until fully oxidised. If much fat is present, 20 or 30 c.c. of nitric acid should be added from the commencement.

The nitric acid and the bulk of the sulphuric acid are then expelled by concentration to about 30 or 40 c.c., and the residue is finally diluted with 30 times its volume of water. The liquid is then ready for treatment with hydrogen sulphide, &c., or it may be at once introduced into the Marsh apparatus.

L. DE K.

Detection and Estimation of Boric Acid in Butter. M. MONHAUPT (*Chem. Zeit.*, 1905, 29, 362—363).—The usual plan is to saponify the butter with alcoholic potassium hydroxide and then to

test for boric acid in the ash as usual. For quantitative purposes, this process is, however, extremely inconvenient. The author recommends the following method.

A large quantity of the sample is shaken in a separating funnel, or in a wash-bottle, with water at 60°. The aqueous liquid is then removed, rendered alkaline with potassium hydroxide, and evaporated to dryness. The residue is ignited to destroy the organic matters and the ash is extracted with hot water. When cold, the solution is made up to a definite bulk, and in an aliquot part the boric acid is titrated by the glycerol method.

L. DE K.

Estimation of Carbon in Ferrosilicon. K. JENE (*Chem. Zeit.*, 1905, 29, 309).—The finely-powdered sample spread out in a thin layer is burnt with the usual precautions in a current of oxygen and the carbon dioxide formed is absorbed in a weighed potash-apparatus.

L. DE K.

Estimation of Carbon Dioxide in Air. W. MACKIE (*J. Hygiene*, 1905, 5, 201—222).—A handy method is described which gives better results than was anticipated. It depends on the view that equal quantities of alkali hydroxide in solution, of equal depth and surface area, will be neutralised by the carbon dioxide in a given atmosphere in equal times, and the times necessary for neutralisation will be inversely as the amounts of carbon dioxide in the atmosphere to which they are exposed. A number of equal spots of an alkaline solution coloured with phenolphthalein are exposed to the atmosphere under investigation, and the time required for decolorisation noted. If s is the strength of the solution, x the time in minutes of the discharge of colour, sf/x = vols. of carbon dioxide in 10,000 parts: f being a constant factor.

W. D. H.

New Reagent for Potassium. EUGENIO P. ALVAREZ (*Chem. News*, 1905, 91, 146).—When sodium 1-amino- β -naphthol-6-sulphonate in saturated aqueous solution is shaken with solutions of potassium salts, brilliant, white, orthorhombic plates of the potassium salt separate—rapidly with 10 or 5 per cent. solutions of potassium chloride, but slowly with weaker ones, whilst more dilute solutions require some hours. Ammonium salts are not precipitated by the reagent, neither are magnesium salts in presence of excess of ammonium chloride.

D. A. L.

Testing Effervescing Sodium Tartrate, so-called "Effervescing Citrate of Magnesia." E. BARONI and G. B. GUIDI (*Chem. Centr.*, 1905, ii, 902—903; from *Giorn. Farm. Chim.*, 54, 49—52).—Ten grams of the sample introduced into a 4 cm.-wide 250 c.c. cylinder containing 90 c.c. of water at 15° should cause a lather reaching up to the 240 mark within 10 minutes. When treated with acids, 9 per cent. of carbon dioxide should be evolved. The sample should be free from reducing sugars, sulphates, borates, and [abroad] even from magnesium compounds.

L. DE K.

Behaviour of Carbonates and Hydroxides towards Saturated Solutions of Potassium and Ammonium Carbonates. CARL ARNOLD (*Ber.*, 1905, 38, 1173—1176).—On account of the varying statements in most analytical text-books, the author tabulates the solubility of the freshly precipitated carbonates and hydroxides of most of the common metals in saturated solutions of potassium and ammonium carbonates. A source of error has been the employment of solutions of ammonium carbonate containing too large a proportion of ammonium hydroxide.

W. A. D.

Estimation of Zinc in Blendes and other Natural and Artificial Products. (The late) H. SALVIN PATTINSON and GEORGE C. REDPATH (*J. Soc. Chem. Ind.*, 1905, 24, 228—230).—Results obtained by three separate methods for the estimation of zinc in blendes, &c., are given, the object of the investigation being to show that the discrepancies which sometimes occur when the same sample is analysed by different analysts are mostly due to imperfect separation of the zinc, rather than to errors in the estimation itself. The authors prefer a modification of Von Schulz and Low's method, according to which the ore is treated with hydrochloric acid and evaporated to dryness after adding nitric acid. The residue is heated, cooled, and extracted with a solution containing 1 gram of ammonium chloride and 3 to 5 c.c. of ammonia for each gram of ore. The extracted residue is redissolved in hydrochloric acid, evaporated, and extracted a second time. If manganese is present, it is precipitated by adding bromine to the ammoniacal solution, collected on a filter, and redissolved in hydrochloric acid. Any zinc carried down with the manganese is precipitated from this acid solution by hydrogen sulphide in the presence of ammonium acetate. The zinc sulphide is then redissolved and added to the main solution, which is titrated with potassium ferrocyanide solution, using uranium acetate as indicator. Lewis's method (*Abstr.*, 1903, ii, 454) gives results agreeing with those obtained by the above process, as does also Von Berg's method, in which the ore is dissolved in hydrochloric and nitric acids, evaporated with sulphuric acid, and filtered. The filtrate is nearly neutralised with ammonia and ammonium carbonate is added until a permanent precipitate is obtained. The latter is just redissolved by sulphuric acid, ammonium chloroacetate and chloroacetic acid are added, and the zinc is precipitated with hydrogen sulphide.

W. P. S.

Lead in Pharmacopœial Chemicals. CHARLES A. HILL (*Chemist and Druggist*, 1905, 66, 388—391).—The following quantities of lead were found in samples of "purest" chemicals, the results being expressed in parts per million : phosphoric acid of sp. gr. 1.75, 1 to 14 ; hydrochloric acid, 1 to 6 ; nitric acid, 1 to 75 ; sulphuric acid, usually less than 15 but occasionally more ; acetic acid, 0 to 3 ; potassium acetate, traces ; sodium acetate, heavy traces ; ammonium carbonate, up to 120 ; borax, 1 to 12 ; boric acid, 2 to 50 ; tartaric acid, 4 to 10 ; citric acid, usually less than 5 ; potassium hydrogen tartrate, mere traces to 4 ; potassium sodium tartrate, 5 to 10 ; magnesium oxide (light), 10 to 30 ; magnesium oxide (heavy), 30 to 300 ; magnesium

carbonate (light), 8 to 20 ; magnesium carbonate (heavy), 20 to 200 ; magnesium sulphate, 2 to 6 ; other sodium and potassium salts, 0 to 15 ; glycerol and lactic acid, none.

W. P. S.

Detection and Estimation of Lead in Cream of Tartar. L. and J. GADAIS (*Ann. Chim. anal.*, 1905, 10, 98—101).—Five hundred grams of the sample are dissolved in 400 c.c. of water and 300 c.c. of pure hydrochloric acid and, after adding 0.15 gram of copper in the form of nitrate, the metals are precipitated by a current of hydrogen sulphide. The sulphides are collected and washed and then dissolved in 8 c.c. of nitric acid. The whole is diluted with water, boiled, filtered, and evaporated to about 25 c.c. After transferring to a suitable apparatus and diluting with another 25 c.c. of water, the liquid is submitted to electrolysis.

The lead deposits as peroxide on the anode and may be weighed as such. It may be identified by the fine blue colour generated on moistening with an acetic acid solution of tetramethyldiaminodiphenylmethane. For a mere qualitative test, it is sufficient to operate on only 100 grams of the sample.

L. DE K.

Assay of White Metal. DINAN (*Chem. Centr.*, 1905, i, 770 ; *Mon. Sci.*, [iv], 19, 92—94).—One gram of the alloy is oxidised with nitric acid, the dry residue is moistened with nitric acid and boiled with water. The insoluble residue is boiled with 150 c.c. of water, 7 grams of oxalic acid, and 7 grams of ammonium oxalate for 45 minutes. The turbid liquid is then diluted to 250 c.c. and treated at 90—95° for 2—3 hours with a current of hydrogen sulphide. The tin which remains in solution is recovered by electrolysis after expelling the hydrogen sulphide and adding another 10 grams of oxalic acid.

The sulphides are boiled with 15 c.c. of water and 2 grams of potassium hydroxide ; the antimony dissolves and is recovered electrolytically after adding 50 c.c. of a saturated solution of sodium monosulphide.

The undissolved sulphides of copper and lead are treated as usual, the lead being separated as sulphate and the copper being recovered from the filtrate by electrolysis after addition of nitric acid.

L. DE K.

Estimation of Acids combined with Aluminium. OTTO SCHMATOLLA (*Ber.*, 1905, 38, 985—989).—It is shown that slightly different results are obtained by titrating a solution of aluminium sulphate with sodium carbonate and with sodium hydroxide respectively ; in the latter case, a small proportion of the sulphuric acid is retained by the precipitated aluminium hydroxide in the form of a basic sulphate. The influence of neutral salts on the titration is also discussed. The best procedure seems to be to titrate the aluminium sulphate solution with sodium carbonate, maintaining the solution at the boiling point throughout, phenolphthalein being employed as indicator ; allowance has to be made for the small quantity of sulphuric acid retained by the precipitate, which is a constant quantity. In the case of the acetate, nitrate, and chloride, on

account of the volatility of the acid, an excess of the alkali is added, the excess being then estimated. W. A. D.

Qualitative Reactions for Columbium and Tantalum. PETR G. MELIKOFF and EUGEN ELTSCHANINOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 99—103).—The potassium salt of fluoropercolumbic acid, in presence of a small quantity of hydrogen peroxide, is coloured yellow by sulphuric acid. A concentrated aqueous solution of potassium percolumbate is coloured yellow by 60—70 per cent. sulphuric acid. These reactions render it possible to detect traces of columbium in tantalum preparations. T. H. P.

Estimation of Bismuth by Precipitation as Molybdate. EDMUND H. MILLER and FREDERICK VAN DYKE CRUSER (*J. Amer. Chem. Soc.*, 1905, **27**, 116—121).—The nitric acid solution of the bismuth is mixed with a large excess of the ordinary ammonium molybdate reagent and the liquid is neutralised with dilute ammonia, using congo-red as indicator; a drop or two of dilute nitric acid is then added until the colour is lilac. The whole is diluted to about 200 c.c. and slowly heated to 50—60°. The precipitated bismuth ammonium molybdate is collected on a platinum Gooch crucible and thoroughly washed with a 3 per cent. solution of ammonium nitrate. After drying in an air-bath at 160°, the precipitate is moistened with a few drops of strong nitric acid and ignited over a bunsen flame, taking care the temperature does not exceed a dull red heat. The treatment with acid and subsequent ignition being repeated a few times, the mass will be of a light yellow colour, and have the composition $\text{Bi}_2\text{O}_3 \cdot 4\text{MoO}_3$. L. DE K.

Optical Examination of Naphtha and of its Distillation Products. II. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 85—91).—The rotatory power may be used as a means of distinguishing different naphthas from one another, and also from vegetable and animal oils. The rotation of naphtha products increases with the sp. gr., and all fractions up to machine oil can be read in a 200 mm. tube if they are pure. This method of examination hence possesses the character of a colorimetric method. The rotation of naphtha products represents a well-defined physico-chemical constant, and is unaffected by the action of heat or time. Purification diminishes to some extent the rotation of crude naphtha distillates. The rotations of a number of light and dark naphthas both of Baku and Grosny origin have been measured and the numbers tabulated. T. H. P.

Detection and Estimation of Fusel Oil. T. TAKAHASHI (*Bul. Coll. Agr. Tōkyō*, 1905, **6**, 436—438).—The liquid (4—6 c.c.) is treated with 5—10 drops of a 1—2 per cent. alcoholic solution of benzaldehyde, anisaldehyde, or *o*-hydroxybenzaldehyde, and then with an equal volume of sulphuric acid. In presence of fusel oil, benzaldehyde gives a red colour above a yellow layer; anisaldehyde, brownish-yellow under green and yellow layers, the former changing to red, the latter

to blue and brownish-purple; *o*-hydroxybenzaldehyde gives a red layer with a purple layer above.

For estimating the amount of fusel oil, the liquid (10 c.c.) is poured into a small cylinder and treated with 2 c.c. of 1 per cent. anisaldehyde in alcohol and 20 c.c. of sulphuric acid. A solution of fusel oil of known strength in 15 per cent. alcohol is similarly treated. The colours produced at intervals of 20 seconds, 1, 3, and 10 minutes are observed. A table is given showing the differences when 0.0001, 0.001, 0.01, and 0.1 per cent. of fusel oil are present (compare Komarowski, *Abstr.*, 1903, ii, 700).

N. H. J. M.

Colorimetric Estimation of Higher Alcohols in Brandies.

XAVIER ROCQUES (*Ann. Chim. anal.*, 1905, 10, 103–108. Compare *Compt. rend.*, 140, 511).—In this method, which depends on the colour developed by the higher alcohols when heated in alcoholic solution with sulphuric acid, the mixture should be heated at 130°, as at this temperature identical colorations are obtained with *isobutyl* and *amyl* alcohols, whilst considerable divergences occur at lower temperatures.

L. DE K.

New General Colour Reagent of the Polyphenols, their Iso-merides, and Higher Organic Compounds. EUGENIO P. ALVAREZ (*Chem. News*, 1905, 91, 125).—0.4–0.5 gram of the polyphenol is added to 0.2 gram of yellow, granulated, perfectly dry sodium peroxide in a porcelain dish and treated with 5 c.c. of absolute alcohol; the dish is gently agitated, the colour effects noted, and after 5 or 6 minutes 15 c.c. of cold water are added. Catechol gives a fugitive pale pink, changing into green and finally brown, and with water the liquid becomes permanently reddish-brown. Resorcinol assumes a very pale yellow, turning green, which becomes more decided and permanent with water. Quinol produces an intense reddish-yellow which the water changes to a persistent orange. Pyrogallol shows a reddish-brown or dull red, becoming intense red with a yellow margin when water is added, and changing to orange in 24 hours. Hydroxyquinol gives a reddish-violet which deepens and turns brown, whilst the peroxide blackens; with water, the liquid becomes yellow. Phloroglucinol develops a bluish-violet, which increases in intensity with water, but subsequently fades. Orcinol yields pink, becoming persistent rose-red with water. Homocatechol colours the alcohol bluish-violet which changes at once to red, and with water, to reddish-brown with a yellow margin. With thymoquinol, the alcohol assumes an orange colour which with water turns red and slowly fades. Some incidental effects are also noted.

D. A. L.

Estimation of Dextrose in Urine. H. L. VISSER (*Chem. Centr.*, 1905, i, 776; from *Pharm. Weekblad.*, 42, 121–124).—The urine is first clarified by means of basic lead nitrate and 10 c.c. of the filtrate are then boiled with 2 c.c. of Fehling's solution. The cuprous oxide is collected on a cotton-wool filter and weighed as such.

L. DE K.

Reactions of Carbohydrates. RUDOLF ADLER and OSKAR ADLER (*Pflüger's Archiv*, 1905, 106, 323—328).—The characteristic red coloration due to furfurylaniline acetate is obtained when a small amount of a pentose is added to a boiling mixture of equal parts of aniline and glacial acetic acid. This serves as a simple qualitative test for pentoses, as other carbohydrates do not give this coloration in the course of a short time. The heptoses are exceptional in their behaviour as they also yield furfuraldehyde and therefore give a red coloration.

Seliwanoff's red coloration (Abstr., 1887, 459) is also obtained when lævulose or any ketose is warmed for a short time with resorcinol and acetic acid containing a few drops of hydrochloric acid. The reaction is much more trustworthy than the original test, as aldoses do not give a coloration under these conditions.

Similarly Tollens' reactions with orcinol or phloroglucinol may be carried out with hot acetic acid solutions containing a few drops of hydrochloric acid.

When dextrose is heated with aniline and acetic acid, a reddish-brown coloration is developed, and this on further heating changes to an intense green. A similar reaction appears to be given by all hexoses or polysaccharides, which readily yield hexoses.

Other bases may be substituted for aniline, and different colorations are thus obtained. J. J. S.

Detection of Sawdust in Flour and Bread. PIETRO PAGANINI (*Chem. Centr.*, 1905, i, 695—696; from *Giorn. Farm. Chim.*, 54, 5—11).—The flour is spread out in a thin layer and moistened first with a 0.2 per cent. aqueous solution of *p*-phenylenediamine and then with acetic acid. The woody fragments at once assume an orange-red colour, whilst the bran fragments remain colourless. The test is also applicable to adulterated maize flour and to thin slices of bread. L. DE K.

Estimation of Acetone by the Iodoform Process. GUSTAV KEPPELER (*Zeit. angew. Chem.*, 1905, 18, 464—465).—In reference to an article by Vaubel and Scheurer (this vol., ii, 291), the author states that Messinger's process is quite satisfactory if the following points are observed. The iodine solution should be added slowly with constant stirring and in decided excess, and some 5 minutes should elapse before titrating with thiosulphate. L. DE K.

Analysis of Wine Vinegar. A. FROEHNER (*Zeit. Nahr. Genussm.*, 1905, 9, 361—363).—Analyses of three samples of wine vinegar are given, the results on the whole agreeing with those previously published by Farnsteiner (Abstr., 1899, ii, 705). Lactic acid is generally a constituent of this class of vinegar, and its detection and determination serve as criteria in ascertaining whether or not a vinegar is wine vinegar. The amounts of lactic acid found in the above-mentioned samples were 0.221, 0.247, and 0.215 gram per 100 c.c., whilst the total acidities (as acetic acid) were 8.47, 9.03, and 7.83 respectively. W. P. S.

Estimation of Volatile Acids in Wine. KARL WINDISCH and THEODOR ROETTGEN (*Zeit. Nahr. Genussm.*, 1905, 9, 278—279).—Methods which depend on the prolonged evaporation of the wine, or in which the residue is heated to a high temperature (Abstr., 1879, 290; 1882, 999, 1235), the volatile acids being obtained by difference, give untrustworthy results. Direct distillation in a current of steam yields better results (Abstr., 1884, 641), but the process is tedious owing to the slow volatility of certain of the acids present in wine. Attention is again drawn to the indirect method recently published (Abstr., 1905, ii, 212) for estimating these acids. W. P. S.

Volatility of Lactic Acid with Water Vapours. FRANZ URTZ (*Chem. Zeit.*, 1905, 29, 363—364).—The author has proved experimentally that lactic acid is volatilised with aqueous vapours, particularly when the solutions become more concentrated, but this volatility is not sufficient to admit of a quantitative estimation of the acid. L. DE K.

The Composition of Lombardy Milk. G. BILLITZ (*Milchw. Zentr.*, 1905, 1, 113—122).—A regulation having recently (1902) been made at Milan that all milk sold shall contain at least 12 per cent. of dry solids, consisting of 3 per cent. of fat and 9 per cent. of non-fatty solids, or else be described as "watered" milk, the author gives the results of analyses of 187,610 samples of Lombardy milk, the investigation extending over the years 1892—1902 inclusive. The average results for the whole period were: sp. gr., 1.0315; fat, 3.55 per cent.; non-fatty solids, 8.81 per cent. The poorest milk was yielded by a herd of 50 cows in March, 1899, the results being: sp. gr., 1.0306; fat, 2.70 per cent.; non-fatty solids, 8.45 per cent.; whilst the richest milk was obtained in December, 1902, from a herd of 80 cows: sp. gr., 1.0326; fat, 4.10 per cent.; non-fatty solids, 9.23 per cent. From this it will be seen that the limits laid down by the Milan authorities are too stringent. W. P. S.

Amount of Water in Butters of Various Origin, and their Reichert-Meissl Numbers. HERMANN THEODOR (*Chem. Zeit.*, 1905, 29, 309).—A table giving the percentage of water contained in butters of various origin. As regards their Reichert-Meissl number, the lowest of which (25) is given by a Dutch butter, it must be remembered that the English method gives results which are about one degree below those obtained by the German process. L. DE K.

Sinacid-Butyrometry. MÖLKEREITECHN. INST. SICHLER & RICHTER, LEIPZIG (*Milchw. Zentr.*, 1905, 1, 71—78. Compare Du Roi and Köhler, this vol., ii, 125).—A reply to various criticisms of the method, which is stated to be trustworthy and rapid. N. H. J. M.

Influence of the Duration of Boiling on the Saponification Value of Beeswax. SCHWARZ (*Zeit. öffentl. Chem.*, 1905, 11, 6—8).—The results of the experiments described show that, by boiling 3 grams of beeswax with 25 c.c. of $N/2$ alcoholic potassium hydroxide

solution for 1 hour, complete saponification is effected, and that no advantage is gained by prolonging the time of boiling to 2 or 3 hours. Boiling for 1 hour is sufficient even when the wax is adulterated with solid paraffin. A further quantity of neutral alcohol should be added before titration to prevent dissociation by the standard acid employed. This addition of alcohol is also necessary when the saponification value is determined by Henrique's cold saponification process. W. P. S.

Bromine Absorption of Fats. FERNAND TELLE (*J. Pharm. Chim.*, 1905, 21, 183—187).—Bromine absorption of fats and oils is recommended instead of iodine absorption, as the former is not only more easy of execution, but gives constant and trustworthy results. A table is given containing the bromine figures of 25 oils and fats.

L. DE K.

Detection of Palm Oil when used as a Colouring Matter in Oils and Fats. CHARLES A. CRAMPTON and FRANK D. SIMONS (*J. Amer. Chem. Soc.*, 1905, 27, 270—274).—The authors communicate two methods for the detection of palm oil, or rather of its colouring matter, in fats and oils.

First Method.—One hundred c.c. of the fat (melted at 70° and filtered) are dissolved in 300 c.c. of light petroleum and shaken with 50 c.c. of 0.5 per cent. potassium hydroxide. The aqueous solution is drawn off, acidified with hydrochloric acid, and shaken with 10 c.c. of carbon tetrachloride. A portion of this is then tested as follows: two c.c. of 1 part of crystallised phenol dissolved in 2 parts of carbon tetrachloride are added to it in a porcelain crucible and 5 drops of hydrobromic acid of 1.19 sp. gr. are stirred in. The almost immediate development of a bluish-green colour is indicative of palm oil.

Second Method.—Ten c.c. of the melted and filtered fat are shaken with an equal volume of acetic anhydride; a drop of sulphuric acid of sp. gr. 1.53 is added, and the whole shaken for a few seconds. If palm oil is present, the lower layers will be found to be coloured blue with a tinge of green.

L. DE K.

Analysis of India-rubber Wares. WERNER ESCH and ABRAHAM CHWOLLES (*Chem. Centr.*, 1905, i, 190; from *Gummi Zeit.*, 19, 125—126).—A criticism of Pontio's method (*Ann. Chim. anal.*, 1902, 7, 13). It is not advisable to substitute alcohol for acetone, as it dissolves but little of the unsaponifiable fats. In order to dissolve any asphalt, Henriques and Weber use nitrobenzene, whilst Pontio uses a mixture of 60 parts of oil of spike and 40 parts of acetone; the authors cannot approve of this solvent. They also call attention to an error in the literature and state that Pontio's solvent used for the extraction of vulcanised india-rubber consists of 85 per cent. of sulphur-free petroleum and 15 per cent. of benzene.

L. DE K.

Detection and Estimation of Bitumen in Gutta Percha. MAURICE PONTIO (*Ann. Chim. anal.*, 1905, 10, 57—58).—After digesting the sample of gutta percha in absolute alcohol to ascertain the amount of resins, it is extracted in a suitable apparatus

for 12 hours with boiling ether and the residue is then collected, dried, and weighed. If the sample contains bitumen, the residue contains the natural impurities of the gutta *plus* 62/100ths of the added bitumen. To see whether this is really present, the mass is further extracted with carbon disulphide or boiling toluene and by reweighing the undissolved matter the bitumen is found by difference. Its weight multiplied by 100/62 represents the total bitumen.

L. DE K.

Estimation of Quinine in Cinchona Barks. VIGNERON (*J. Pharm. Chim.*, 1905, 21, 180—183).—The mixed alkaloids, obtained as usual from 25 grams of bark, are treated with twenty times their weight of ether, about six small pieces of pumice soaked in alcohol are added, and the whole is kept for 6 hours with occasional shaking. The ether is decanted on to a filter and the residue extracted again with the same volume of fresh ether for 12 hours. The mixed ethereal solutions are allowed to evaporate, and the residue is dissolved in 5 c.c. of alcohol and 100 c.c. of water previously saturated with quinine sulphate. The whole is heated on the water-bath to expel the alcohol and ether, and during this time the alkaloids are converted into normal sulphates by neutralisation with normal sulphuric acid, using tincture of logwood as indicator.

When cold, the separated quinine sulphate which, however, generally contains some cinchonidine sulphate, is collected, washed with solution of quinine sulphate, dried at 100°, and weighed as anhydrous sulphate. To ascertain the true amount of quinine, an aliquot portion is dissolved in hot water previously saturated in the cold with quinine chromate, and precipitated according to De Vrij's method with potassium chromate. Seventy-six parts of quinine chromate dried at 100° = 75 parts of the dried sulphate. The filtrate should be tested with sodium hydroxide to ascertain whether cinchonidine is really present.

L. DE K.

Estimation of the Active Principles of Alder Bark. JULES WARIN (*J. Pharm. Chim.*, 1905, 21, 253—263).—The principle of the method is as follows: when treating the powder of alder bark with a half per cent. solution of sodium hydroxide, a red solution is obtained, which may then be compared colorimetrically with an alkaline solution of emodin of known strength. Better results are, however, obtained by diluting a measured portion of the alkaline solution to such an extent that its colour is no longer visible when viewed through a solution of nickel chloride placed in another tube of the same size. This nickel solution contains exactly 1 gram of metallic nickel in 100 c.c., and neutralises the colour of 0.001 gram of emodin dissolved in 100 c.c. of alkaline water. For minute particulars necessary to ensure success, the original article should be consulted. The result gives the valuable constituents expressed as emodin.

L. DE K.

Analysis of Tanning Materials with Exfoliated Alumina. HANS WISLICENUS (*Zeit. anal. Chem.*, 1905, 44, 96—106).—The voluminous alumina obtained by the atmospheric oxidation of amal-

ganated aluminium possesses the property of removing from solution 25—45 per cent. of its weight of tannin, and may therefore be used with advantage in place of hide powder. The tannin precipitate is not decomposed by washing with hot water, alcohol, or ether; on the other hand, the sugars and other non-tanning constituents of an extract are easily washed out. The alumina can be regenerated by incinerating the precipitate, and its adsorptive power is not impaired by ignition. The amount of tannin precipitated cannot be ascertained by weighing the precipitate, but is obtained by difference from the dry residues of the solution before and after precipitation. Duplicate estimations with this precipitant show greater concordance than is attainable with hide powder. In preparing the alumina, the presence of water should be avoided as far as possible, and the oxide should finally be separated from unoxidised metal by elutriation with ether. It is ignited before use. M. J. S.

Preparation and Estimation of Lecithin. HERBERT E. ROAF and E. S. EDIE (*Thompson, Yates, and Johnston Lab. Rep., Liverpool*, 1905, 6, 201—205).—Egg yolks are repeatedly extracted with alcohol; the alcohol from the united extracts is distilled off under reduced pressure. To the syrupy mass so obtained, a little ether is added and the liquid precipitated with acetone. The precipitate is heated on a steam-bath to remove ether and acetone and weighed, or the lecithin in it determined by phosphorus estimation. W. D. H.

Estimation of Albumin in Barley. R. HEERDE and E. BUSCH (*Chem. Centr.*, 1905, i, 299—300, 300; from *Woch. Brauerei*, 21, 779—780, 830—832).—Using the whole grains for Kjeldahl's method leads to serious discrepancies. The barley should therefore be ground to a fine flour, of which 2 grams are taken for analysis. After heating with 30 c.c. of sulphuric acid and 1 gram of mercury for 10 minutes, 15 grams of potassium sulphate are added. The mixture requires boiling for 35 minutes. When distilling off the ammonia, the receiver should be kept very cool, so as to prevent loss of ammonia.

NEUMANN states that there is no loss of ammonia even if the contents of the receiver should get overheated. On using a large Jena glass flask, there is no need for transferring the acid liquid to another distilling flask.

In the later papers, the respective authors reaffirm the antagonistic views put forth in the first. L. DE K.

General and Physical Chemistry.

Chemistry of Phosphorescing Sulphides of the Alkaline Earths. PERCY WAENTIG (*Zeit. physikal. Chem.*, 1905, **51**, 435—472. Compare Abstr., 1903, ii, 625).—The author's experiments confirm the view that the marked phosphorescence exhibited by the sulphides of the alkaline earths is conditioned by the presence in solid solution of a small quantity of certain heavy metals. A purified sample of strontium sulphide has been obtained exhibiting only a very faint blue phosphorescence, and this residual phosphorescence was traced to the presence of iron. Platinum, even in traces, also appears to have the power of causing phosphorescence in the sulphides of the alkaline earths. The intensity of the phosphorescence increases with the concentration of heavy metal present so long as the latter is dissolved to a homogeneous solid solution. The solubility of these heavy metals increases with rising temperature, and is very small at the ordinary temperature; all phosphorescing sulphides, therefore, which have been obtained by heating an alkaline earth carbonate and sulphur with the nitrate or sulphate of the heavy metal are to be regarded at the ordinary temperature as supersaturated solutions. Hence many factors are to be considered in the preparation of a highly phosphorescent sulphide, such as the temperature at which the sulphide is to be prepared, the duration of the heating, and the rate of cooling. Allowing for the influence of these various factors, the author has prepared sulphides, the phosphorescent efficiency of which is greater than that of the products obtained by the usual methods. The presence of a small quantity of a fusible salt is favourable for the production of a highly phosphorescent sulphide, because (1) it promotes the solution of the heavy metal in the sulphide, (2) it hinders the separation of the heavy metal during the process of cooling.

When the sulphides of the alkaline earths are ground in a mortar, they become coloured and lose, to a large extent at least, their phosphorescent power. The colour assumed varies with the sulphide used, and depends neither on the heavy metal present nor on the original phosphorescence colour. The coloured powder is unstable compared with the original white phosphorescent material. The change can be effected in either direction at one and the same temperature.

Intermittent illumination over a period of several months does not apparently lead to any diminution of phosphorescent power: so far, therefore, there is no indication that a chemical change is involved.

J. C. P.

The Light emitted by Crystals of Arsenious Oxide. DESIRÉ GERNEZ (*Compt. rend.*, 1905, **140**, 1134—1136).—The luminous effect which accompanies the formation of octahedral crystals of arsenious oxide from hydrochloric acid solutions of the vitreous variety is due to the rupture of the crystals induced by contact with one another, and

can be produced artificially by crushing the crystals against the walls of the vessel with a metal rod; the phenomenon is therefore one of triboluminescence. The author finds that triboluminescent crystals are deposited from hydrochloric acid solutions of vitreous arsenious oxide made at the ordinary temperature or from hydrochloric acid solutions of the ordinary powdered octahedral arsenious oxide made at boiling point (compare Guinchant, following abstracts), and, provided they remain unbroken, the crystals retain this property for a period of over four months.

M. A. W.

Luminescence of Arsenious Oxide. JOSEPH GUINCHANT (*Compt. rend.*, 1905, 140, 1101).—The luminescence of arsenious oxide depends solely on the concentration of hydrogen chloride in the liquid, and is to be attributed to the reversible chemical change, $\text{As}_2\text{O}_3 + 6\text{HCl} = 2\text{AsCl}_3 + 3\text{H}_2\text{O}$.

H. M. D.

Triboluminescence of Arsenious Oxide. JOSEPH GUINCHANT (*Compt. rend.*, 1905, 140, 1170—1171. Compare preceding abstracts).—The luminescence of arsenious oxide crystals is due to the rupture attending their transformation into the cubic modification, and has no action on an electroscope. The light thus produced gives a continuous visible spectrum in which the yellow and green radiations predominate; these radiations are photochemically active, producing in four minutes, at a distance of a few centimetres, the same photographic effect as the blue flame of a Bunsen burner at a distance of one metre.

The rest of the paper is occupied with a description of the luminous phenomena which are produced when hypobromites or hypochlorites are reduced by carbamide, oxamide, ammonium thiocyanate, asparagine, uric acid, or ammonia under suitable conditions of concentration. The light emitted has feeble photochemical properties and arises from the explosive decomposition of the nitrogen chloride which is formed during the first phase of the reaction between carbamide and a hypochlorite. If concentrated solutions of hypochlorous acid and carbamide are mixed, there is no immediate action, but after a few minutes oily drops of nitrogen chloride are formed, which in the presence of oil of turpentine explode with an evolution of light, and the decomposition is also brought about by alkalis.

The bubbles of hydrogen evolved when sodium amalgam is thrown into a concentrated solution of sodium hypobromite are surrounded by a luminous zone.

M. A. W.

Radioactivity as an Atomic Property. HERBERT N. MCCOY (*J. Amer. Chem. Soc.*, 1905, 27, 391—403).—A number of experiments are described in which measurements of radioactivity of uranium compounds were carried out by means of the electroscope. The compounds examined were the oxide, U_3O_8 , the oxalate, $\text{UO}_2\cdot\text{C}_2\text{O}_4\cdot 3\text{H}_2\text{O}$, and ammonium uranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$. The results are plotted as curves, and show that the effective activity of layers of uranium compounds of sufficient thickness to show the maximum α -ray activity depends not only on the uranium content, but also on the coefficient of absorption of the rays by the radioactive substance itself. A method

has been worked out for the determination of such absorption coefficients. It is shown that, when absorption is taken into account, the total α -ray activity of any uranium compound is strictly proportional to the percentage of uranium which it contains, and the theory that radioactivity is an atomic property is thus confirmed.

E. G.

Properties of Radium in Minute Quantities. A. S. EVE (*Phil. Mag.*, 1905, [vi], 9, 708—711).—Voller found recently (see *Physikal. Zeit.*, 1904) that radium distributed on a plate in minute quantities and exposed to the air disappeared and decayed in a few days or weeks, and that the activity of radium thinly distributed over a small surface was not proportional to the mass present, but was relatively greater for small quantities. The author shows that when similar experiments are made in a closed vessel, no disappearance can be detected, and the activity is at least approximately, and probably accurately, proportional to the mass present.

A supplementary note by ERNEST RUTHERFORD (*ibid.*, 711—712) emphasises these points, and suggests that the decrease of activity observed by Voller has nothing to do with any actual change in the rate of disintegration of the radium, but is due to the escape of the radium from the plate into the surrounding gas. A similar loss would probably be observed even with inactive matter if it were deposited in such minute amount.

J. C. P.

The Constant for the Rate of Decay of Radium Emanation. OTTO SACKUR (*Ber.*, 1905, 38, 1753—1756. Compare Curie, Abstr., 1903, ii, 50; Rutherford, *ibid.*, 347).—Curie finds that the constant for the rate of decay of the radium emanation is 2.02×10^{-6} , whereas Rutherford gives 2.16×10^{-6} . The author has measured the rate of decay by the method of Rutherford and Soddy, and finds the value 2.08×10^{-6} . The activity of the emanation diminishes in 92.6 hours to one-half of its original value.

A. MCK.

Radioactivity of the Gastein Thermal Springs. HEINRICH MACHE (*Monatsh.*, 1905, 26, 349—372. Compare Curie and Laborde, Abstr., 1904, ii, 461; Elster and Geitel, Abstr., 1904, ii, 695).—The radioactive emanation obtained in varying, but mostly considerable, amount from the gases and water of the Gastein thermal springs, a list of which is given, has a rate of decay which is approximately equal to that of the radium emanation, as is also that of the induced radioactivity to the activity induced by radium emanation. The radioactive substance which produces the emanation obtained from the gases and water is found in the reissacherite of the deposits from the thermal springs. This mineral, which has a radioactivity approximately equal to that of uranyl nitrate, contains manganese dioxide, ferric oxide, calcium carbonate, barium, and strontium, but neither sulphuric acid nor uranium; on separation, the radioactive substance is obtained along with the barium and is presumably radium.

G. Y.

Radioactivity of some Deep Well and Mineral Waters. HERMANN SCHLUNDT and RICHARD B. MOORE (*J. Physical Chem.*, 1905, 9, 320—332).—The authors have tested the radioactivity of a number of deep well waters and expressed the values by means of the standard suggested by Boltwood (*Abstr.*, 1904, ii, 666), that is, in terms of the unit representing the amount of radium emanation associated with 1×10^{-4} grams of uranium in a natural mineral. The emanation dissolved in the water was obtained by boiling the water and collecting the dissolved gas. The values for the radioactivity obtained varied from 0.17 to 4.45 units per litre of water. It was found from the rate of decay that the radioactive properties were due to radium emanation. It was also found that a little less than one-half the total emanation was liberated before boiling, this being also the case for water rendered active by radium emanation. L. M. J.

Excited Activity of Thorium. Miss J. M. W. SLATER (*Phil. Mag.*, 1905, [vi], 9, 628—644).—The results of the investigation are summarised as follows. The two stages in the disintegration of thorium-excited activity, the existence of which has been already indicated by theoretical considerations, are both present on any surface exposed to thorium emanation. The constituent with the slower rate of decay (half value in 11 hours) is first formed, and may be referred to as thorium *A*. The thorium *B* formed from it is responsible for the radiation emitted, and has a more rapid rate of decay (half value in 55 minutes). Both substances are partly volatilised on exposure to the cathode ray discharge, thorium *B* being more volatile than thorium *A* in these circumstances. The cause of the volatilisation is partly a direct action of the cathode rays, and partly a sputtering of the active matter, analogous to that observed with metallic cathodes. Under the influence of heat, thorium *A* is more volatile than thorium *B*; when an active wire is kept for a few minutes at a dull red heat, the former constituent is removed and nearly pure thorium *B* is then left on the wire. J. C. P.

Radioactivity of Thorium. OTTO SACKUR (*Ber.*, 1905, 38, 1756—1761).—The author has measured the rate of decay of the emanation of the product obtained by Hahn by the fractionation of radium barium bromide, and from the values obtained concludes that thorium emanation was evolved from a new radioactive element present in Hahn's product.

The possibility of thorium itself being inactive, whilst its radioactivity is due to the presence of some other substance, is discussed.

The oxalate obtained from thorianite was converted into oxide and then into chloride, which, when submitted to fractional sublimation, did not indicate any separation of the radioactive component.

Barium hydroxide solution was gradually added to a solution of the sulphate obtained from the oxalate and the precipitated barium sulphate was found to be strongly radioactive, a result due to the presence of thorium X.

Attempts were also made to prove the presence of a new element by electrolytic methods, which did not lead to the separation of an

element of constant radioactivity, but indicated that solutions of thorium from thorianite and other minerals behave on electrolysis like dilute solutions of a new element which is strongly radioactive.

A. McK.

Ionic Sizes in Relation to the Conductivity of Electrolytes. WILLIAM R. BOUSFIELD (*Proc. Roy. Soc.*, 1905, 74, 563—564).—Starting with the hypothesis that the ions of an electrolyte consist of molecular aggregates largely composed of water molecules, the size of an ion depending on the amount of combined water and being a function of temperature and concentration, the author deduces the following expression for the true coefficient of ionisation in the case of potassium chloride, $\alpha = \Lambda/\Lambda_{\infty} \cdot 1/f \cdot 1/(1 + 3.33h^{-3})$, where f is the fluidity of the solution and h is the "hydration," that is, the ratio of the molecules of water present to the molecules of the solvent. With this coefficient of ionisation, van't Hoff's dilution law, modified by substituting the "hydration" of the solute for its concentration, gives accurate agreement with experimental results over a wide range.

The water entering into combination with the ion is probably abstracted from the solvent largely as "trihydrol" or "hydrol," according to the temperature, and enters into combination with the ion as "dihydrol," thus causing contraction. The ionic volumes calculated from the conductivities on the above hypothesis are in agreement with the solution volumes calculated from the densities. For isothermal concentration changes, the ionic volume decreases as the solution volume increases, that is, with increasing water combination there is increasing contraction, a result which was to be anticipated. But in the case of temperature changes at constant concentration there is increasing water combination with diminishing contraction. This result, however, may be explained by reference to the variation with temperature of the proportions of trihydrol and dihydrol. On the assumption that the attack of the ions on trihydrol and dihydrol is in proportion to their concentrations at the temperatures considered, the volume changes deduced from the conductivities are shown to agree with the volume changes deduced from the densities.

A new variety of viscosity apparatus is described, and measurements of the viscosities and densities of potassium chloride solutions from 0—21 per cent. concentration are recorded.

J. C. P.

Electroaffinity Differences between Valency Stages and their Oxidation Equilibria. II. Mutual Relationships of the Valency Stages of Thallium and the Oxidation Power of Oxygen. JAMES F. SPENCER and RICHARD ABEGG (*Zeit. anorg. Chem.*, 1905, 44, 379—407. Compare Abegg, this vol., ii, 155).—Potential measurements of solutions of thallous and thallic salts with platinum electrodes were made against a 1/10 *N* calomel electrode ($\epsilon_h = -0.336$ volt)³ at 25° by the compensation method. At first the same result could not be attained by the use of two different electrodes, although the result after some time was identical. Thallic salts tend to pass into thallous salts, according to the equation $Tl^{III} \rightarrow Tl^I = 1.199 + 0.029 \log Tl^{III}/Tl^I$.

The dilution of a mixture of thallous and thallic salts has, in the case of the sulphate and nitrate, no influence of the *E.M.F.*, that is, the ratio of the concentration of thallous to thallic salt is constant, and both stages are strongly ionised.

The tendency of an ion (*i*) to undergo transformation into another ion (*o*), exhibiting a valency *n* times less than the former, is expressed in volts by the equation $\epsilon_i \rightarrow_o = P + 0.059/n \log i/o$, where *P* is a constant expressing the tendency for the transition of the *i* into the *o* valency stage, where the concentrations of the ions are identical. For the transition of thallic into thallous chloride, this constant lies nearer the reduction end of the series of electromotive forces than for the nitrate and sulphate, and this is changed on dilution in the direction of the greater tendency to oxidation.

The tendency of the thallic ion to form complexes with the following anions increases in the sequence, Cl', tartrate, acetate, CNO', (CO₂)₂'', Br', NO₂', I', CNS', SO₃'', CN', S₂O₃''.

The hydrolytic reaction, $\text{Ti}(\text{NO}_3)_3 + 3\text{H}_2\text{O} = \text{Ti}(\text{OH})_3 + 3\text{HNO}_3$, is reversible, and gives the constant for the law of mass action,

$$(\text{HNO}_3)^3/\text{Ti}(\text{NO}_3)_3 = 13.6.$$

The solubility product for thallic hydroxide is $L = 10^{-52.83}$.

The solubility of thallic hydroxide is $10^{-13.52}$ molar.

Oxygen oxidises thallous nitrate to the extent of about 2 per cent. until equilibrium is attained, platinum being the catalyst.

The oxidation potential of oxygen is 1.1385 ± 0.001 volt.

Thallic and thallous salts are in equilibrium with thallium, when the ratio of the concentrations Ti'''/Ti' is $10^{-52.2}$.

A *résumé* of the potentials measured is quoted.

A. McK.

Electromotive Force between Metals and Solutions of their Salts in Water and Methyl Alcohol. GIACOMO CARRARA and L. D'AGOSTINI (*Gazzetta*, 1905, 35, i, 132—144).—The authors have measured, by Poggendorff's method, the *E.M.F.* of a number of elements of the type $\text{Hg} - \text{HgCl} - n\text{KCl} - n\text{KNO}_3 - \text{AgNO}_3 - \text{Ag}$, using the metals copper, silver, cadmium, and zinc, and from the results obtained have calculated the absolute potentials between the metals and their salt solutions, and also the solution tensions of the metals. In methyl alcohol, the potential differences between the metals and their solutions are, if they are positive, smaller than, and, if they are negative, greater than, the corresponding values for aqueous solutions. Assuming that the electrolytic pressure of solutions of metals is independent of the solvent, it follows that the organic solvent gives solutions of electrolytes in which the osmotic pressure of the metallic ions is smaller than that of the corresponding aqueous solutions. The difference must, to a great extent, be attributed to the less dissociation of the substance dissolved in the solvent with a less ionising power, and, indeed, the contact potentials of the methyl alcohol solutions tend, in some measure, to approximate to those of aqueous solutions as the dilution is increased. The tensions of the metals in the two solvents are in the same order, but their absolute values are very different in the two cases; the ratio between the values in aqueous

and methyl-alcoholic solution is 1.3 for zinc, 2.2 for cadmium, 0.85 for copper, and 1 for silver.

For cadmium nitrate in methyl-alcoholic solution, the potential differences are small, whilst measurements of the elevation of boiling point show that this salt has a degree of dissociation in methyl alcohol of the same order of magnitude as in water. The electrolytic solution pressure must hence vary with the solvent. The authors explain this by supposing that the electrostriction, and therefore the alteration of the solvent by the ions, is different in different solvents. T. H. P.

Dissociation of Ternary Electrolytes. KARL DRUCKER (*Zeit. Elektrochem.*, 1905, 11, 211—215).—The determination of the concentration of a single ion in the solution of a ternary salt by means of an isohydric solution of a suitable binary salt (Kümmel, this vol., ii, 226) is only applicable when no complex ions are formed from the binary and ternary salts. It also assumes that the law of mass action applies to the solutions used. The author prefers a method which he described some years ago (*Abstr.*, 1902, ii, 3). By means of it, he calculates the concentration of the single ion B in solutions of salts of the type AB_2 , and compares the numbers so obtained with those calculated from the electrical conductivity on the assumption that only the simple ions A and B are formed. The result is that when the transference numbers are independent of the concentration the agreement is good, which would indicate that the assumption of simple dissociation is warranted, whereas in cases in which the transference number changes with the concentration, the agreement is bad, especially in stronger solutions, which would point to the formation of complex ions. T. E.

Dissociation of Cadmium Iodide. JAMES W. MCBAIN (*Zeit. Elektrochem.*, 1905, 11, 215—223).—A compilation of results of previous observers relating to the electrical conductivity, freezing point, and transference numbers of solutions of cadmium iodide, from which it is shown that very dilute solutions of this salt contain the ions Cd^{++} and I^- , whereas very concentrated solutions contain Cd^{++} and CdI_3^- . The details of the calculations cannot be abstracted briefly. T. E.

Diamagnetism of Bismuth. ANATOLE LEDUC (*Compt. rend.*, 1905, 140, 1022—1023).—Although bismuth forms cubic crystals belonging to the regular system, there are reasons for supposing that a sphere cut from a crystal of the metal would take up a definite orientation when brought into a magnetic field. The question has been subjected to experiment in the following way. Small spherical glass bulbs of 2 cm. diameter were filled with molten bismuth, and the metal allowed to solidify whilst the bulbs were under the influence of a strong magnetic field. If the crystalline spheres of bismuth are then suspended freely in the same magnetic field, they take up the same orientation as that which they had at the moment of solidification of the metal. If the magnetic field is cut off and the bulbs are made

to rotate about the axis of suspension, the motion is at once stopped when the magnetic field is established, and the bulbs are found to be orientated as at the time of crystallisation.

H. M. D.

Comparison of the Platinum Scale of Temperature with the Normal Scale at Temperatures between 444° and -190° , with Notes on Constant Temperatures below the Melting Point of Ice. MORRIS W. TRAVERS and ALFRED G. C. GWYER (*Proc. Roy. Soc.*, 1905, 528—538).—The authors have compared the platinum and hydrogen thermometers at -190° (liquid air), -78.2° (solid carbon dioxide and alcohol), and 32.38° (transition temperature of sodium sulphate). For points between 30° and -190° , Callendar and Griffiths' parabolic formula may be used to calculate the difference (Δ) between the platinum scale of temperature and the scale of the gas thermometer, δ being taken as 1.90; the maximum error in the calculation of Δ is then probably not greater than 0.2° at about -100° , but the formula cannot be employed except for interpolation. A standard scale of temperature, based on Callendar's three fixed points, would, supposing standard wire to be used and δ taken = 1.5, lead to absurd results at low temperatures, and the converse may be said of the authors' observations.

J. C. P.

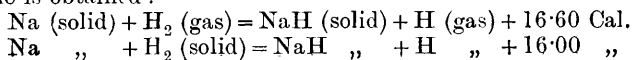
Dependence of Free Energy on Temperature. JOSEPH E. TREVOR (*J. Physical Chem.*, 1905, 9, 299—310).—A mathematical paper dealing chiefly with a hypothesis of Richards in a paper on atomic volumes (*Abstr.*, 1903, ii, 132). This hypothesis, as stated by Richards, is that "the change of free energy with temperature has a fundamental connection with the change of total energy with temperature," the connection being expressed $d\Delta f/d\theta = -M.d\Delta e/d\theta$. The author shows that this is equivalent to the hypothesis that isothermal changes of specific heat are proportional to the $1/M$ th power of the temperature, that is, $\Delta c_2 = A.\theta^{1/M}$. The principles of thermodynamics, however, do not appear to bear upon the possibility of this relationship.

L. M. J.

Heat of Vaporisation of Liquefied Gases. EMILE MATHIAS (*Compt. rend.*, 1905, 140, 1174—1176. Compare *Abstr.*, 1888, 773).—A theoretical paper.

M. A. W.

Heat of Formation of Sodium Hydride; Acidity of the Hydrogen Molecule. ROBERT DE FORCRAND (*Compt. rend.*, 1905, 140, 990—992. Compare *Abstr.*, 1900, ii, 528).—Sodium hydride was prepared by heating the metal in pure hydrogen at 375 — 380° . The heat of solution of the hydride in water, measured with quantities varying from 7 to 38 mg., was found equal to 25.80 Cal. (mean of four experiments). Combining this result with the heat of solution of metallic sodium in water (42.40 Cal.), the heat of formation of sodium hydride is obtained:



The latter number represents the value of the acidity of the molecule of solid hydrogen.

The coefficient of acidity of the atom of hydrogen has been previously given (*loc. cit.*) as 18.43 Cal. The difference between 18.43 and 16.00 is supposed by the author to be due to the influence exerted by the second atom of hydrogen on the neutralisation of the first by sodium. The acidity of the first atom is on this account diminished, and the heat disengagement is smaller.

H. M. D.

An Empirical Relationship between the Densities of Two Liquids. K. SCHAPOSCHNIKOFF (*Zeit. physikal. Chem.*, 1905, 51, 542—546).—If d_T and $d_{T'}$ are the densities of two liquids under the pressure of their own vapour at two temperatures T and T' , such that $T - T' = T_K - T'_K$ (T_K and T'_K being the respective critical temperatures), then the relation between the densities is given by the equation $d_T = n.d_{T'} + b$, where n and b are constants for each pair of substances. With the help of already available data, the formula is tested and found satisfactory for the following pairs of liquids: (1) benzene and stannic chloride; (2) heptane and fluorobenzene; (3) pentane and heptane; (4) pentane and ethyl alcohol; (5) pentane and carbon dioxide. The same formula is applicable to the densities of the saturated vapours as shown in the two cases: (1) pentane and carbon dioxide; (2) pentane and heptane. The densities of liquids under the pressure of their own vapour and the densities of saturated vapours are purely functions of the temperature; that is, $d = f(T)$. Combining this with the empirical relationship given above, the author deduces the equation $(d' + a)/(d'_K + a) = \phi[(T' + c)/(T'_K + c)]$, in which the function ϕ is the same for all substances. This is a generalised form of van der Waals' equation.

J. C. P.

Determination of Volume Change on Liquefaction. A. HESS (*Chem. Centr.*, 1905, i, 1071; from *Physikal. Zeit.*, 6, 186—188).—The substance under investigation is placed in a beaker which is suspended by means of a Jolly spring balance in an electrically-heated thermostat, arranged in such a manner that convection currents are avoided. Thermocouples immersed in the beaker and in the surrounding bath indicate the temperature. The readings of the balance, as the temperature changes, are continuously recorded by means of a mirror rotating about a vertical axis. The liquid in the thermostat must be freed from dissolved gases, and the substance, which should almost fill the beaker, must be sufficiently small to ensure homogeneity and uniformity of temper. For solid, yellow phosphorus at its melting point (44.5°), the specific volume 0.55399 was obtained; for the liquid at the same temperature, 0.057305. The increase in volume on liquefaction is 3.44 per cent.

H. M. D.

Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure. LORD RAYLEIGH (*Phil. Trans.*, 1905, A 204, 351—372. Compare *Abstr.*, 1901, ii, 542).—Details are given of the methods used in the work already described (*Abstr.*, 1904, ii, 313), and some fresh results are recorded. The correction

factors at about 13° (see *loc. cit.*) for carbon dioxide and nitrous oxide are 0.99518 and 0.99422 respectively. For ammonia at about 10° the ratio of *pv.* at 0.5 atmosphere to the corresponding value at 1.0 atmosphere is 1.00632.

J. C. P.

Fundamental Functions of One-component Ideal-constituent Gases. JAMES M. BELL and JOSEPH E. TREVOR (*J. Physical Chem.*, 1905, 9, 179—209).—A mathematical paper in which the authors first recapitulate the Gibbsian theory as applied to dissociation equilibrium between unimolecular and bimolecular gaseous forms of a one-component substance. The authors extend the Gibbsian equation and derive characteristic equations for the pressure, molecular volume, the thermodynamic potential and free energy and their derived functions. A large number of equations are deduced, from which the following may be noted. The increase of dissociation per degree at constant pressure is proportional to Qp/θ^2 where Qp is the molecular heat of dissociation at constant pressure and θ is the absolute temperature. A similar proportionality obtained also at constant volume. The heat capacity at constant pressure or volume is investigated and the work and heat integrals for isothermal paths or paths of constant dissociation are determined. These allow of comparison with the experimental results of Berthelot and Ogier for the heat of cooling of given masses of nitrogen peroxide. The agreement is quite satisfactory.

L. M. J.

Abstract and Concrete Conceptions (Osmotic Pressure and Thermodynamic Potential). JOHANNES J. VAN LAAR (*Chem. Centr.*, 1905, i, 1067; from *Chem. Weekblad*, 2, 143—156. Compare this vol., ii, 234).—Mainly polemical. The agreement of the osmotic pressure with the simple gas laws is only apparent. The equations for the osmotic pressure, $\pi = RT[c + (\frac{1}{2} - a)c^2]$, and for the pressure of a gas, $p = RT(c - \lambda c^2)$, are quite different except when the limiting condition $c = 0$ (infinite dilution) is reached.

In the theoretical treatment of chemical systems, the employment of osmotic pressure instead of thermodynamic potential on account of the abstract nature of the latter conception is unjustifiable. Other conceptions in general use are equally abstract. A comparison is made between thermodynamic potential and electric potential. Both determine an internal condition which is only recognisable by its consequences. Osmotic pressure, lowering of freezing point, and lowering of vapour pressure are secondary consequences of a condition determined primarily by the thermodynamic potential.

H. M. D.

Influence of One Substance on the Solubility of Another Substance. FRIEDRICH HOFFMANN and K. LANGBECK (*Zeit. physikal. Chem.*, 1905, 51, 385—434).—The authors have determined the solubilities of benzoic, salicylic, and *o*-nitrobenzoic acids as these are affected by various electrolytes and non-electrolytes.

At 25° , dextrose is practically without effect on the solubility of benzoic acid, but at 45° the solubility of the acid increases slightly as

the dextrose concentration increases. In solutions of sodium and potassium chlorides and nitrates, benzoic acid becomes less soluble as the salt concentration increases, and the effect of the salts is more marked at 45° than at 25°. The relative influence of the various salts is in accordance with Rothmund's rules (Abstr., 1900, ii, 467).

The solubility of salicylic acid in dextrose solutions increases regularly with the concentration of the latter, and the increase at 35° is the same as at 25°. Ethyl and isobutyl alcohols, especially the latter, raise the solubility of salicylic acid to a marked extent, and the increase in both cases is more marked at 35° than at 25°. With the electrolytes, on the other hand, the solubility of salicylic acid is first raised and then lowered as the salt concentration increases—a peculiar characteristic that is still more definite in the case of the stronger *o*-nitrobenzoic acid. When the percentage change of solubility of the acid is plotted against the salt concentration, maxima are observed for each curve, and the curve for 35° invariably lies below the curve for 25°. Dextrose lowers the solubility of *o*-nitrobenzoic acid, the percentage diminution being approximately proportional to the dextrose concentration; the temperature-coefficient, however, for dextrose is the opposite of that for the electrolytes.

On the basis of Jahn's theory (Abstr., 1902, ii, 597), formulæ are established from which the solubilities of the three acids in the various solutions can be calculated from the solubilities in pure water. The agreement between the calculated and the observed values is very good for the non-electrolytic solutions, but is incomplete in the other case, owing probably to insufficient data regarding the dissociation of the electrolytes involved.

The solubilities of the acids in water are as follows, the numbers indicating grams of acid per 1000 grams of saturated solution: benzoic acid, 3·4009 at 25°, 6·6702 at 45°; salicylic acid, 2·2062 at 25°, 3·197 at 35°; *o*-nitrobenzoic acid, 7·3156 at 25°, 10·537 at 35°. J. C. P.

Solubility and Dissociation of Double Salts in Water.

IV and V. EBERHARD RIMBACH and A. GREWE (*Ber.*, 1905, **38**, 1553—1564, 1564—1572. Compare Abstr., 1898, ii, 158; 1902, ii, 306; 1904, ii, 264).—The double salt, $\text{CdBr}_2 \cdot \text{KBr} \cdot \text{H}_2\text{O}$ ($\frac{1}{2}\text{H}_2\text{O}$; Hauer, *Wien. Akad. Ber.*, 15, 23), forms rhombic prisms [$a:b:c = 0.4592:1:1$]; the solubility determinations give values agreeing with $P(112.5^\circ/0.4^\circ) = 55.108 + 0.218t$, and show that the salt is not decomposed by water within that interval of temperature. Contrary to Eder's (*Dingler's Journ.*, 1876, 189) and Tassilly's statement (Abstr., 1899, ii, 747), the double salt, $\text{CdBr}_2 \cdot \text{NH}_4\text{Br}$, is anhydrous; it is not dissociated on solution in water at 1—110.1°, and has the solubility $P(110^\circ/1^\circ) = 54.47 + 0.197t$.

The double salt, $\text{CdBr}_2 \cdot \text{RbBr}$, forms anhydrous crystals and has $P(107^\circ/0^\circ) = 35.34 + 0.393t$.

Solubility determinations with rubidium bromide give the value $P(114^\circ/0.5^\circ) = 48.63 + 0.1751t$. The following values were calculated from solubility determinations by other authors: for KBr , $P(100^\circ/0^\circ) = 36.192 + 0.1543t$; for NH_4Br , $P(100^\circ/10^\circ) = 38.958 + 0.1768t$; for CdBr_2 , $P(100^\circ/36^\circ) = 59.583 + 0.0183t$; $(36^\circ/0^\circ) = 37.803 + 0.6319t$.

These results agree with the rule that the value dP/dt is greater for double salts than for their constituents.

The double salt, $\text{CdBr}_2 \cdot 4\text{NH}_4\text{Br}$, formed from a solution of its components containing excess of cadmium bromide, separates in hexagonal plates [$a:c = 1:0.6269$]; when shaken with water at from 0.8° to 123.5° , it partly decomposes, the solution containing an excess of cadmium bromide, the solid, the unchanged salt and ammonium bromide; the transformation point is passed by 160° .

The double salt, $\text{CdBr}_2 \cdot 4\text{KBr}$ (Eder, *loc. cit.*; Hauer, *loc. cit.*), cannot be formed from a solution of its components at temperatures up to 160° .

The double salt, $\text{CdBr}_2 \cdot 4\text{RbBr}$, crystallises in hexagonal plates [$a:c = 1:0.6231$]; the salt is isomorphous with the corresponding ammonium salt; the solubility determinations give the value $P(115^\circ/0^\circ) = 50.88 + 0.2637t$.

With alkali iodides, cadmium iodide forms the two series of salts, $\text{CdI}_2 \cdot \text{M'I}$ and $\text{CdI}_2 \cdot 2\text{M'I} \cdot 2\text{H}_2\text{O}$; the latter forms large, transparent, hygroscopic crystals.

It has been shown that double salts which, when shaken with water, form incongruent saturated solutions containing an excess of one component are not decomposed by a solution of that component. It is now found that the excess of the one component necessary to form the double salt may be replaced by other substances having the same anion. Thus the dissociation of $\text{CdCl}_2 \cdot 4\text{KCl}$ by water is diminished by the presence of hydrochloric acid or lithium, calcium or magnesium chloride, and when these salts are present in certain concentrations no dissociation of the double salt takes place; the effective molecular percentage concentration at 16° for CaCl_2 is 0.1887, for LiCl 0.4483, for HCl 0.8828. Similarly with the double salt, $\text{CdCl}_2 \cdot 4\text{RbCl}$, the incongruent saturated solution of which contains an excess of 12.83 mols. of RbCl over each mol. $\text{CdCl}_2 \cdot 4\text{RbCl}$, the minimum effective molecular percentage concentration for CaCl_2 is over 4.59, for LiCl over 19.4, for HCl over 29.8.

The double salt, $\text{CdCl}_2 \cdot 4\text{NH}_4\text{Cl}$, is obtained from solutions of its components containing hydrochloric acid, lithium, calcium, or magnesium chloride. The dissociation of the double salt, $\text{CdBr}_2 \cdot 4\text{NH}_4\text{Br}$, which forms a saturated solution containing an excess of cadmium bromide, is not affected by the presence of hydrobromic acid or lithium, calcium, magnesium, nickel, or cobalt bromides, but the pure double salt is obtained by mixing solutions of its components and zinc bromide. The double salt, $\text{UO}_2\text{SO}_4 \cdot 2\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, is completely dissociated on recrystallisation from dilute sulphuric acid, the solution depositing $\text{UO}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$.

G. Y.

Mixed Crystals in Systems of Three Substances. II. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1905, 51, 547—576. Compare this vol., ii, 154).—A theoretical paper. J. C. P.

A Rule in Chemical Dynamics. JOH. PLOTNIKOFF (*Zeit. physikal. Chem.*, 1905, 51, 603—608).—The curves obtained by plotting reaction velocity-coefficients against temperature are similar to those representing the course of the reaction. The latter are logarithmic curves,

and similarity between the two sets of curves would mean that the change of the velocity-coefficient with temperature is proportional to the velocity-coefficient itself: that is, $dk/dt = ak$. The integration of this leads to $a = (\log k_1 - \log k_2)/(t_1 - t_2)$, a formula which is tested with satisfactory results in some thirty cases. Since the equilibrium constant is the quotient of two velocity-coefficients, an analogous formula may be deduced for the equilibrium constant, namely, $\beta = (\log K_1 - \log K_2)/(t_1 - t_2)$. The applicability of the latter formula is tested in a few cases with satisfactory results. J. C. P.

Equilibrium between a Nitrogen Base and Organic Acids in Various Solvents. HERBERT F. SILL (*Zeit. physikal. Chem.*, 1905, 51, 577—602).—The equilibrium constant k_e for the reaction (cinchonine salt) \rightleftharpoons (cinchonine cation) + (acid anion) and the equilibrium constant k_a for the reaction (cinchonine salt) \rightleftharpoons (free cinchonine) + (free acid) have both been determined for a series of organic acids (benzoic, *p*-hydroxybenzoic, and butyric acids, trichlorophenol, *o*- and *p*-nitrophenol) in methyl- and ethyl-alcoholic solution. The total base (free and combined) in solution was determined by titration, and as the solutions were kept saturated with cinchonine the amount of free base was known. The molecular conductivity of the solutions was determined, and λ_∞ was calculated from the corresponding value for water (see Völlmer, *Abstr.*, 1894, ii, 339); thus the degree of dissociation of the cinchonine salt could be ascertained. The values obtained for k_e in each case are satisfactorily constant, that is, Ostwald's dilution law is fulfilled in the case of these cinchonine salts, although it should be noted that the author's experiments do not cover a wide range of concentration. The values of k_a for different concentrations are also satisfactorily constant. The affinity constants of the various acids in alcoholic solution are proportional to the product $k_a k_e$, and run approximately parallel to the affinity constants of the same acids in water; *p*-nitrophenol, however, is a marked exception to this rule, a fact in harmony with Hantzsch's view that this substance is a pseudo-acid (see *Abstr.*, 1900, i, 94). The value of k_e for the methyl-alcoholic solutions stands in a constant ratio to the corresponding value for the ethyl-alcoholic solutions, to which rule *p*-nitrophenol is again an exception.

For a given solvent, the values of k_e vary but slightly with the acid used, so that the value of k_a alone is really a measure of the strength of the acid. This is confirmed not only for the methyl- and ethyl-alcoholic solutions, but also for some solutions in *isoamyl* alcohol and acetone. J. C. P.

Reaction-velocities in Heterogeneous Systems: with Particular Reference to Enzyme Actions. GEORGE SENTER (*J. Physical Chem.*, 1905, 9, 311—320).—The view has been put forward by Nernst that at the surface of separation of two phases, equilibrium is very rapidly established, and that what is actually measured as the rate of reaction is, in reality, the rate of subsequent diffusion (*Abstr.*, 1904, ii, 315). Consequently doubts were cast on the van't Hoff method of determining the order of a reaction. The results of Brunner

(*ibid.*) in the case of velocities of dissolution were in agreement with these views, whilst experiments of Heber (Abstr., 1904, ii, 309) showed that, although in some cases electrical reduction proceeds with measurable velocity towards equilibrium, yet in other cases diffusion velocities are obtained. It is probable, therefore, that the relative parts played by diffusion and the actual chemical change must be determined in each particular case. The author suggests the three following criteria: (1) relation between diffusive power and reaction-velocity; (2) effects of substances which alter viscosity; (3) temperature-coefficient; and applies these in an investigation on the velocity of enzyme reactions, based on the results of previous observers. Although the data are insufficient for definite conclusions, they tend to show that in these cases the velocities are true reaction-velocities, and that the formula and theory suggested by Herzog are not valid (Abstr., 1904, ii, 506).
L. M. J.

Enzymatic Fermentation from the Point of View of Chemical Dynamics. HANS EULER (*Zeit. physiol. Chem.*, 1905, 44, 53—73. Compare Aberson, Abstr., 1903, ii, 445; Herzog, *ibid.*, ii, 230).—The enzyme used was zymase, prepared by Büchner's method from a bottom yeast, rendered poor in glycogen by drying for 3—4 hours at 40° in thin layers. The yeast extract, which was only very slightly optically active, was mixed with solutions of pure dextrose and 0.2 c.c. of toluene and the amounts of carbon dioxide evolved after given times determined gravimetrically or gasometrically.

The results have been used for calculating the velocity constant, $K = 1/t \log a/a - x$, where a = the amount of carbon dioxide in grams or c.c. evolved during time t , and $a - x$ the amount of carbon dioxide which would be evolved supposing the whole of the remaining dextrose became transformed into alcohol and carbon dioxide. The value for K is fairly constant for any set of experiments, but shows a tendency to diminish as t increases.

The results of numerous experiments show:

(1) That the constant becomes smaller when the concentration of the original sugar solution is increased, but the relationship is not one of inverse proportionality.

(2) That the velocity is not directly proportional to the zymase concentration, but increases more quickly. The exponent n in the equation $n = (\log K_1 - \log K_2) / (\log c_1 - \log c_2)$ becomes smaller and approximates closer to 1 as the concentration of the zymase is increased.

(3) That when the amount of extract and of sugar are kept constant and the amount of water varied, the constant is almost directly proportional to the concentration.
J. J. S.

Chemical Combination. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 1153—1159. Compare this vol., ii, 308).—Nitrogen and hydrogen do not combine to form ammonia when heated in sealed silica tubes at 1300° for an hour and cooled either rapidly or gradually, and similarly negative results are obtained when the gases are heated in the presence of hydrogen chloride at temperatures above

800°; both the hydrogen and nitrogen escape by diffusion through the walls of the tube, the hydrogen more rapidly than the nitrogen, but the hydrogen chloride does not begin to diffuse until a temperature of 1400—1500° is reached. Ammonia is completely dissociated into hydrogen and nitrogen when heated at 1300°; at 600° 5.5 per cent., and at 800° 10 per cent. of the gas is dissociated; ammonium chloride is dissociated into hydrogen, nitrogen, and hydrogen chloride at 1300°, the hydrogen chloride undergoing no dissociation even at 1400—1500°. When hydrogen sulphide is heated at 1300° in sealed silica tubes and cooled gradually, the contents of the tube are completely absorbed by a solution of potassium hydroxide, but if the tube be cooled rapidly about 5 per cent. of the residual gas consists of hydrogen, showing that hydrogen sulphide is dissociated at a high temperature. M. A. W.

Anti-oxidation of Solutions of Sodium Sulphite and Anti-oxidising Agents. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], 33, 444—454).—Anti-oxidation is the term applied to the phenomenon of the retardation of the rate of oxidation of aqueous solutions of sodium sulphite by air, induced by the addition of minute quantities of reducing (anti-oxidising) agents. The following substances are arranged in order of decreasing activity: quinol, *p*-aminophenol hydrochloride, glycine, *p*-phenylenediamine, catechol, “metol,” “metoquinone,” diaminophenol hydrochloride, “aduril,” “edinal,” and “eikonogen.” Acetone behaves in the reverse way. The effect is independent of time, temperature, light, and the concentration both of the sulphite and the anti-oxidising agent, but is diminished by the addition of alkaline substances, acetone or formaldehyde. The action appears to be catalytic in character. It is pointed out that a solution of sodium sulphite may be preserved for a prolonged period by the addition of a small quantity of one of the more active anti-oxidising agents.

T. A. H.

Contact Phenomena in the Flame under the Influence of Solids. A. A. BAIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 156—169).—The author finds that solid substances, such as platinum, quartz, and porcelain, when heated in one and the same flame, assume various temperatures differing from the temperature of the flame itself; the difference may amount to several hundreds of degrees. The temperature to which a solid becomes heated in a flame depends on the contact properties of the solid and on the relation between its surface and its volume. The method of determining the temperature of a flame by the temperature to which a solid body is heated in it is hence quite inaccurate, and the true temperature of a flame is at present an unknown quantity. The differences in the luminosities of different solids when heated in one and the same flame are dependent on the fact that the substances assume different temperatures.

T. H. P.

Rôle of Diffusion in the Catalysis of Hydrogen Peroxide by Colloidal Platinum. GEORGE SENTER (*Proc. Roy. Soc.*, 1905, 74, 566—574).—A discussion of the points raised by Sand (this vol., ii,

233). The deviations from the simple logarithmic formula in the catalytic decomposition of hydrogen peroxide by colloidal platinum are probably due to disturbances caused by convection currents. It is also shown that when the velocity constant, calculated on Nernst's diffusion hypothesis, is great compared with the chemical velocity constant, increased convection can produce no appreciable effect on the observed reaction-velocity. Since, in the case under consideration, increased convection does modify the observed reaction-velocity, there must be some error in the assumptions leading to the conclusion that the diffusion velocity constant is great compared with the chemical velocity constant. The error probably lies in the assumption that the whole platinum surface is, under ordinary conditions, active towards hydrogen peroxide.

The considerations which favour Nernst's diffusion hypothesis as applied to the platinum catalysis are the small value of the temperature-coefficient and the fact that the deviations from the simple logarithmic law in catalysis by platinum have their exact analogy in the hæmase catalysis.

J. C. P.

Isodimorphism. FRÉDÉRIC WALLERANT (*Compt. rend.*, 1905, 140, 1045—1046).—Thallous nitrate and ammonium nitrate are both polymorphous, the former crystallising in cubic, rhombohedral, or orthorhombic forms, whilst the latter forms cubic, quadratic, or orthorhombic crystals. The mixed crystals which separate on cooling fused mixtures of the two nitrates have been examined. If the percentage of ammonium nitrate in the fused mass does not exceed 3·2, the mixed crystals which separate resemble thallous nitrate, and assume successively cubic, rhombohedral, and orthorhombic forms on cooling. If the percentage of ammonium nitrate in the fused mass lies between 3·2 and 5·8, then on solidification there seem to be formed two varieties of cubic crystals, one form containing 3·2 per cent., the other 5·8 per cent. of ammonium nitrate. On cooling to 104°, the cubic crystals of the first kind become rhombohedral, whilst those of the second kind are transformed into quadratic crystals. On further cooling, the rhombohedral crystals become orthorhombic at 68°. When the proportion of ammonium nitrate in the fused mixture exceeds 5·8 per cent., the cubic crystals which first separate are transformed into quadratic crystals, but as the proportion of ammonium nitrate increases these are transformed into crystals belonging to the orthorhombic system. Three series of mixed crystals are thus obtained at the ordinary temperature.

H. M. D.

The Eighth Group of the Periodic System. RICHARD ABEGG (*Ber.*, 1905, 38, 1386—1388. Compare Werner, this vol., ii, 308).—Helium, neon, argon, krypton, and xenon, and iron, cobalt, nickel, and the platinum metals are arranged respectively as sub-groups in the eighth group of the periodic system; it is pointed out that from theoretical considerations the two sub-groups of this group must differ greatly from one another, just as the sodium metals differ from copper, silver, and gold. Further, the inert elements of the argon group form a link between the strongly electronegative elements of the seventh

and the electropositive elements of the first groups: the existence of such a group was forecast by Lothar Meyer. E. F. A.

Lecture Experiments [Decomposition of Carbon Dioxide by Magnesium]. KARL BRUNNER (*Ber.*, 1905, 38, 1432).—Magnesium powder is scattered over a flat dish containing solid carbon dioxide, a small amount of burning magnesium is dropped into this; the metal continues to burn and forms a grey cake, which, on treatment with water and hydrochloric acid, leaves a residue of black, flocculent carbon. Aluminium powder burns under the same conditions, some aluminium carbide and oxide being formed. J. J. S.

Quantity of Moisture left in a Gas after its Passage over Phosphoric Oxide. EDWARD W. MORLEY (*J. Chim. Phys.*, 1905, 3, 241—244).—The total quantity of moisture and phosphoric oxide vapour left in 4300 litres of gas dried by the dehydrator was only 0.1 mg.; further experiments to determine the quantities of each, indicated that the whole was phosphoric oxide, but the author does not consider them trustworthy owing to the magnitude of the relative errors. His results show, however, that for any gravimetric work the moisture contained in a gas dried by this dehydrator is quite negligible. L. M. J.

New Filter Tube. H. P. MASON (*Chem. News*, 1905, 91, 180—181).—In this arrangement, the stem is separate from the body of the tube, and is shaped to remain in position at the constricted lower end of the tube body, and to form a ledge upon which a porcelain disc for supporting the filtering material can rest. The stem is slightly longer than the body, and can be used to eject the filter. D. A. L.

Inorganic Chemistry.

Acceleration of the Evolution of Chlorine from Potassium Chlorate and Hydrochloric Acid by the presence of Platinum. H. Sirk (*Zeit. Elektrochem.*, 1905, 11, 261—263).—Sand (this vol., ii, 156) has shown that the reaction between a chlorate and hydrochloric acid takes place slowly, and is represented by the equation $\text{ClO}_3' + 2\text{H}' + 2\text{Cl}' = \text{ClO}' + 2\text{HOCl}$. The hypochlorous acid and hydrochloric acid then react, rapidly producing chlorine. It is shown that this reaction is accelerated by platinum; the acceleration observed depends on the surface of platinum in contact with the solution. The acceleration of the reverse reaction is of importance in the electrolytic production of chlorates with platinum electrodes. T. E.

Action of the Silent Electric Discharge on Chlorine. FRANZ RUSS (*Ber.*, 1905, 38, 1310—1318. Compare Mellor, *Proc.*, 1904, 20, 140, 196).—The “activation” of chlorine, measured by its action on

benzene, is greatest when moist chlorine is exposed to the simultaneous action of light and of a silent electric discharge. The "activation" decreases as the chlorine is dried, and is much less if the action of light or of the silent discharge is omitted. As the action of light is due to the ultra-violet rays, the rate of "activation" is greater in a quartz than in a glass vessel. "Active" chlorine retains its activity for long periods at the ordinary temperature, but is rendered inactive by heating, by the passage of electric sparks, or by treatment with water.

G. Y.

Apparatus to show the Production of Ozone during the Combustion of Coal Gas. LÉON MAQUENNE (*Bull. Soc. chim.*, 1905, [iii], 33, 510—511).—A frame is used carrying four air-gas burners, producing flames from 15 to 20 mm. high. On the edges of each of these flames are placed two small horizontal tubes, and the whole eight tubes are connected to a central "blower." The current of air so produced blows away the ozone and nitrous fumes as soon as they are formed, and the presence of these gases can be detected by the usual tests at a distance of several metres from the apparatus.

T. A. H.

Two Liquid States of Sulphur, S_λ and S_μ , and their Transition Point. ALEXANDER SMITH (*Proc. Roy. Soc. Edin.*, 1905, 25, 588—589).—It is shown that there are two liquid states of sulphur, which are only partially miscible; these are yellow, mobile sulphur (S_λ), predominating from the melting point to 160° , and brown, viscous sulphur (S_μ), prevailing above 160° . The facts demonstrating the existence of these two states are, firstly, the sudden change of viscosity at 160° and the simultaneous marked absorption of heat. Further, it is shown that the curves of solubility of S_λ and S_μ in triphenylmethane and other solvents are quite distinct, the solubility of S_λ increasing, that of S_μ decreasing, with rise of temperature. The coefficient of expansion of S_λ diminishes rapidly from 154° to 160° , that of S_μ increases rapidly from 160° upwards. The point of minimum dilatation is displaced upwards when triphenylmethane is dissolved in the sulphur. The dilatometric method gives no evidence of the existence of Frankenheim's transition point at 250 — 260° .

J. C. P.

Nature of Amorphous Sulphur, and Influence of Foreign Substances on the Phenomena of Supercooling observed when Melted Sulphur is suddenly chilled. ALEXANDER SMITH (*Proc. Roy. Soc. Edin.*, 1905, 25, 590—592. Compare Abstr., 1903, ii, 139, 284, also preceding abstract).—A study of the hardening of plastic sulphur shows that the whole of the amorphous sulphur present cannot be obtained in quasi-solid form because of partial reversion to the soluble form. The sulphur, however, precipitated in presence of concentrated acids yields 100 per cent. of insoluble sulphur. The amounts of insoluble sulphur obtained on chilling common sulphur from various temperatures vary from 4.2 per cent. at 130° to 34 per cent. at 448° . These amounts

are greatly reduced when the sulphur has been heated for a long time at 448° , or for a shorter time in a vacuum, or has been used immediately after recrystallisation, or has been washed with water before being heated; such treatment probably removes the trace of sulphuric acid acquired by the sulphur on exposure to air. To the substances previously mentioned (Abstr., 1903, ii, 139) as favouring the formation of insoluble sulphur, iodine should be added. Sulphur which gives the insoluble form on chilling has the same constitution near the boiling point as sulphur which does not give the insoluble form on chilling. This was deduced from the identity in boiling point under ordinary and reduced pressures, and from the identity of specific gravity. Solubility experiments between 120° and 160° show further that the constitution of the two kinds of sulphur just mentioned is the same also below the transition point 160° . The conclusion is reached that amorphous sulphur is supercooled S_{μ} (see preceding abstract), and the part played by carbon dioxide, ammonia, hydrogen sulphide, sulphur dioxide, iodine, &c., in influencing the amount of insoluble sulphur produced by chilling is probably just a hindering or promoting of the supercooling. J. C. P.

Improved Hydrogen Sulphide Apparatus. AUGUST SCHRIMPF (*Zeit. anal. Chem.*, 1905, 44, 195).—A modified Kipp apparatus, in which the solid reagent is placed in the uppermost bulb and the acid is supplied from an independent elevated tubulated bottle by tubing which passes to the bottom of the lower bulb. M. J. S.

Solubility of Sulphur Dioxide in Water. AUGUST HARPF (*Chem. Centr.*, 1905, i, 1208; from *Chem. Zeitschr.*, 4, 136—137).—The strength of the liquor which runs from the ordinary Schröder tower and the percentage of sulphur dioxide contained in it may vary within very wide limits. These quantities depend on the concentration of the gas, its temperature (t), and the quantity of water (h) with which the gas comes in contact. If g = volume of the gas absorbed, then for 100 parts and at atmospheric pressure, $g = (a.h.v.)/100$.

From a gas containing 10 per cent. by volume of sulphur dioxide at 10° , 1.63 per cent. by weight is dissolved by a litre of water. When the pressure in the tower is increased to five atmospheres, 8.14 per cent. by weight is dissolved. E. W. W.

Explanation of the Action of Strong Sulphuric Acid on Metals. CHARLES M. VAN DEVENTER (*Chem. Centr.*, 1905, i, 992; from *Chem. Weekblad*, 2, 137—140).—When concentrated sulphuric acid acts on metals, it is probable that the initial action consists rather in the formation of oxide, sulphur dioxide, and water, than in the formation of sulphate and hydrogen. According to both theories, the acid acts as an oxidising agent, but no direct proof of the formation of hydrogen has been adduced. Dilute sulphuric acid acts on zinc, but not on copper, silver, or mercury, which are all readily attacked, however, by the concentrated acid. The analogy between the action of carbon or sulphur on concentrated sulphuric acid with that of these elements on nitric acid, and the decomposition of sulphuric acid at

high temperatures into oxygen, water, and sulphur dioxide, lend support to the oxide theory. E. W. W.

Reduction of Tetrathionates to Sulphites by Arsenite and Stannite. AUGUST GUTMANN (*Ber.*, 1905, 38, 1728—1734).—A solution of sodium arsenite in sodium hydroxide acts on sodium tetrathionate according to the equation $\text{Na}_2\text{S}_4\text{O}_6 + 3\text{Na}_3\text{AsO}_3 + 2\text{NaOH} = 2\text{Na}_3\text{AsSO}_3 + \text{Na}_3\text{AsO}_4 + 2\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$. Sodium monothioarsenate, $\text{Na}_3\text{AsSO}_3 \cdot 12\text{H}_2\text{O}$ (*Abstr.*, 1897, ii, 257), is identified by heating its aqueous solution with acids, when sulphur separates and arsenious acid is formed. Sodium monothioarsenate is not formed in an aqueous solution of sodium hydroxide, sodium tetrathionate, and sodium arsenite until the solution is warmed. The amount of arsenate formed was estimated.

Sodium stannite reduces sodium tetrathionate in alkaline solution to sulphite, thiostannate and stannate being also formed. A. McK.

Formation of Ammonia from its Elements. FRITZ HABER and GABRIEL VAN OORDT (*Zeit. anorg. Chem.*, 1905, 44, 341—378).—The determination of the equilibrium between nitrogen, hydrogen, and ammonia at 1020° has been studied more accurately than in the preliminary communication by the same authors (this vol., ii, 159). The free energy of formation of ammonia was calculated; the percentage of ammonia in mixtures of ammonia, nitrogen, and hydrogen in equilibrium under a pressure of 1 atmosphere was, for the temperatures 27°, 327°, 627°, 927°, 1020° respectively, 98·51, 8·72, 0·21, 0·024, 0·012 respectively.

The reversible action, $\text{Ca}_3\text{N}_2 + 3\text{H}_2 \rightleftharpoons 3\text{CaH}_2 + \text{N}_2$, takes place at a red heat, whilst ammonia is also formed. Traces of ammonia are formed during the action of hydrogen on calcium nitride, but not by the action of nitrogen on calcium hydride. The range of temperature within which the intermediate formation of a calcium compound takes place lies too high to enable a convenient synthesis of ammonia to be attained by its aid.

Manganese can be transformed into a nitrogen compound, and then again obtained from the latter by reduction, by the alternate action of nitrogen and hydrogen. The use of manganese as a catalyser in the synthesis of ammonia is suggested.

Experiments to demonstrate the synthesis of ammonia are described. A. McK.

Decomposition of Ammonia at High Temperatures. ALFRED H. WHITE and WM. MELVILLE (*J. Amer. Chem. Soc.*, 1905, 27, 373—386).—The experiments described were undertaken in order to ascertain the influence of change of temperature on the decomposition of ammonia and the effect of diluting the ammonia with one of the products of its decomposition, and with other gases which are generally present in the manufacture of coal gas. The apparatus consisted essentially of a glass combustion tube, through the wide end of which a Le Chatelier pyrometer tube of glazed porcelain was inserted. The gas was passed through the annular space between the pyrometer and

the combustion tube, and its temperature was measured just as it was about to be withdrawn and cooled. In this apparatus, experiments were made at temperatures between 450° and 730° with pure ammonia and with ammonia diluted with hydrogen, nitrogen, carbon monoxide, and water vapour. The results are tabulated and are also plotted as curves.

It is shown that the temperature of initial decomposition of ammonia is about 450° . The proportion of ammonia decomposed does not appear to be affected by dilution with hydrogen or nitrogen so long as the time that each ammonia molecule remains in the tube is not changed; there is therefore no tendency for the nitrogen and hydrogen to recombine. The rate of decomposition is somewhat increased by the presence of carbon monoxide or water vapour. In the presence of carbon monoxide, a small quantity of cyanogen is produced, a larger amount being formed with the dry gases than in the presence of aqueous vapour, but the highest yield obtained in any experiment only amounted to about 4 per cent. of the ammonia decomposed. The decomposition seems to take place almost entirely on the impact of the ammonia molecules on the hot solid surface, a larger proportion being decomposed on a rough than on a smooth surface; thus it has been found that ammonia gas may undergo but slight decomposition when passed through a hot glass tube, whilst in contact with porcelain at the same temperature the decomposition may be 50 times as great.

It is concluded that in the destructive distillation of coal the decomposition of the ammonia may be prevented by keeping the temperature low, and by reducing the time in which the gases remain in contact with hot, rough surfaces like those of coke or fire-clay.

E. G.

New Reactions of Nitroxyl (Dihydroxyammonia). ANGELO ANGELI and FRANCESCO ANGELICO (*Gazzetta*, 1905, 35, i, 152—159. Compare Abstr., 1904, i, 172).—Further study of the reactions of nitroxyl renders it probable that it has the constitution of dihydroxyammonia, $\text{NH}(\text{OH})_2$, or the corresponding anhydride, NHO . Thus, it is formed by the oxidation of hydroxylamine by means of Caro's acid, and hence forms a term in the series of oxidation products of ammonia: ammonia, hydroxylamine, dihydroxyammonia, nitrous acid. Its behaviour resembles in some respects that of hydroxylamine, and in others that of nitrous acid. Thus with aldehydes it gives hydroxamic acids, just as hydroxylamine gives oximes, and dihydroxyammonia and hydroxylamine both act on true nitroso-compounds, giving nitrosohydroxylamines and diazo-compounds respectively. Further, nitrous acid acts on secondary amines, yielding nitrosoamines, whilst dihydroxyammonia and secondary amines give compounds of the type $\text{NRR}'\cdot\text{NH}\cdot\text{OH}$, which lose water and polymerise, forming tetrazones. Also, with mono-substituted hydroxylamines, dihydroxyammonia gives diazo-hydroxides; for instance, with phenylhydroxylamine in presence of α -naphthol, it yields benzeneazo- α -naphthol. This probably completes the number of methods by which diazo-compounds can be prepared. Thus, $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{OH}$ can be obtained from $\text{C}_6\text{H}_5\cdot\text{NH}_2 +$

HNO_2 , $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{OH} + \text{NOH}$, $\text{C}_6\text{H}_5\cdot\text{NO} + \text{NH}_2\cdot\text{OH}$, or $\text{C}_6\text{H}_5\cdot\text{NO}_2 + \text{NH}_3$. So also can phenylnitrosylhydroxylamine be obtained from $\text{C}_6\text{H}_5\cdot\text{NH}_2 + \text{HNO}_3$, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{OH} + \text{HNO}_2$, $\text{C}_6\text{H}_5\cdot\text{NO} + \text{NH}(\text{OH})_2$, or $\text{C}_6\text{H}_5\cdot\text{NO}_2 + \text{NH}_2\cdot\text{OH}$.
T. H. P.

New Method for preparing Oxides of Nitrogen and hence Nitric Acid from Compressed Air by Electric Means. EMILIO ROSSI (*Gazzetta*, 1905, 35, i, 89—110).—An incandescent substance, such as a Nernst lamp, causes the formation of oxides of nitrogen in the air, and if it is placed in an enclosed vessel containing air under pressure and also sulphuric acid, the amount of nitric oxide subsequently obtainable from the acid is large enough to be of importance for the manufacture of nitric or sulphuric acid. Two ampere-hours acting on 1.25 litres of air under 50 atmospheres pressure in a closed vessel containing 8 c.c. of sulphuric acid yields as much as 200 c.c. of nitric oxide.
T. H. P.

Catalytic Decomposition of Arsenic Hydride. GEORG LOCKEMANN (*Zeit. angew. Chem.*, 1905, 18, 491—494).—The decomposition of arsenic hydride is accelerated by the presence of moist cotton or quartz wool. Alcohol has a similar effect. It is shown that cotton wool (or glass wool) is unsuitable for drying purposes in the Marsh test; the progress of the decomposition of arsenic hydride by these catalytic agents was measured. From the figures quoted, it appears that, as the unimolecular reaction represented by the equation $2\text{AsH}_3 = 2\text{As} + 3\text{H}_2$ proceeds, the oxidation of the arsenic hydride gradually diminishes.
A. McK.

Theory of the Velocity of Solution of Arsenious Oxide. ERICH BRUNNER (*Zeit. physikal. Chem.*, 1905, 51, 494—499. Compare Drucker, Abstr., 1901, ii, 376; Brunner, Abstr., 1904, ii, 315).—The author considers that the velocity of solution of arsenious oxide is not governed exclusively either by the rate of diffusion or by the rate of hydration in the solution, but that both factors are involved. On this basis, it is possible to interpret all the observations hitherto made on the velocity of solution of arsenious oxide.
J. C. P.

Permeability of Fused Silica Tubes. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 1159—1162. Compare this vol., ii, 316).—Fused silica tubes with walls 0.7 mm. thick are not permeable to hydrogen at the ordinary temperature, but become so at 800°, whilst at 1300° the diffusion is very marked; hydrogen chloride does not begin to diffuse through the walls of a silica tube below 1400°, neither does carbon dioxide below 1300°; the diffusion of nitrogen is feeble at 1000°, but becomes appreciable at 1300° to 1400°, whilst oxygen diffuses more readily; relative experiments on the rates of diffusion of these two gases show that at 1400° under a pressure of 1.2 atmospheres one-sixth of the initial volume of nitrogen or one-third of the initial volume of oxygen diffuses during one hour. The silica tubes suffer a permanent distension from the effect of the increased internal pressure at the high temperature.
M. A. W.

Coagulation of Colloidal Silicic Acid. II. NICOLA PAPPADÀ (*Gazzetta*, 1905, 35, i, 78—86. Compare Abstr., 1904, ii, 120).—Decinormal, normal, or even stronger solutions of methyl, ethyl, or propyl alcohol, ethylene glycol, glycerol, mannitol, dextrose, lævulose, or sucrose have no coagulating action on a 0.6 per cent. solution of colloidal silica, and have no retarding influence on substances which cause coagulation. The action of the latter substances is due not to the integral molecule or to the anion, but only to the cation. The coagulating action of salts is intimately connected with the positions of the metals in the periodic system; thus caesium is more energetic than rubidium, rubidium than potassium, potassium than sodium, and sodium than lithium; ammonium salts stand very near to those of potassium as regards their coagulating action. The positive ions of salts act catalytically in coagulating colloidal solutions of silica, their action being closely analogous with those of organic ferments. The coagulants are rendered inactive by the presence of traces of acids, whilst the coagulation is favoured by small quantities of substances having a basic reaction. T. H. P.

Behaviour of Hydrofluosilicic Acid with Various Reagents. A. GAWALOWSKI (*Zeit. anal. Chem.*, 1905, 44, 191—194).—An aqueous solution of hydrofluosilicic acid gives precipitates with sulphuric acid, normal and acid potassium chromates, chromic acid, dilute hydrochloric acid, and potassium chlorochromate. Most of these precipitates are soluble in alkalis, but insoluble in acids; that obtained with potassium dichromate is, however, not attacked by cold potassium hydroxide, and as it has a deep yellow colour it might prove serviceable as a pigment. M. J. S.

Liberation of Hydrogen during the Action of Sodium on Mercury. LOUIS KAHLBERG and HERMANN SCHLUNDT (*J. Physical Chem.*, 1905, 9, 257—259).—It was found that when sodium amalgam is formed by the action of sodium on mercury, hydrogen is liberated, and the authors obtained on an average 3.24 c.c. of hydrogen (at 20° and 750 mm. pressure) per gram of sodium. It was found by Lockyer that, when heated, carefully distilled sodium gives off about 20 times its volume of hydrogen. The difference in the amount of hydrogen obtained in the two methods necessitates further inquiry. L. M. J.

Polysulphides. II. FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1905, 44, 431—452. Compare Küster and Heberlein, this vol., ii, 156).—The process of solution of sulphur in sodium sulphide can be followed by potential measurements until the solution is saturated. Between the potential of the platinum electrodes in the solutions of sodium polysulphides, saturated with sulphur, and the dilution of those solutions, simple relationships obtain, which find expression in the Nernst formula. The case is similar when silver electrodes are used.

The potential differences between platinum and silver electrodes were measured in solutions of sodium sulphide, to which sulphur was added in gradually increasing amounts. From the latter measurements, the

concentrations of the sulphur ions (S'') and of free sulphur were calculated.

The hydrolysis and ionisation of such solutions were diminished by the addition of potassium hydroxide and of sodium chloride. Measurements of potential, made after the addition of these substances, afforded a means of calculating the concentration of the sulphur ions, and the results thus obtained were in satisfactory accordance with those calculated by the aid of the law of mass action.

In accordance with the results obtained by purely chemical methods, these electrical measurements show that in the formation of polysulphides by the solution of sulphur in sodium sulphide the sulphur is more firmly combined as far as the formation of the compound Na_2S_4 ; after that stage, the sulphur is not so firmly combined.

A. McK.

Cæsamide. ETIENNE RENGADÉ (*Compt. rend.*, 1905, 140, 1183—1185. Compare this vol., ii, 174).—Cæsium ammonium (compare Moissan, *Abstr.*, 1903, ii, 477) decomposes spontaneously into cæsamide and hydrogen; at the ordinary temperature, the decomposition is gradual, but becomes rapid and complete at 120° ; the *cæsamide* thus formed is a white solid, crystallising from liquid ammonia in small prisms or plates; it melts in a vacuum at about 260° , is readily oxidised with the formation of cæsium nitrite, cæsium hydroxide, and ammonia, and reacts violently with water to form cæsium hydroxide and ammonia. Potassamide behaves similarly to the cæsium compound towards oxygen, whilst sodamide is not attacked by a solution of oxygen in liquid ammonia.

M. A. W.

Position of the Alkali and Alkaline-earth Metals in the Electrochemical Series at High Temperatures. H. DANNEEL and LORENZ STOCKEM (*Zeit. Elektrochem.*, 1905, 11, 209—211).—Calcium is not reduced from the chloride or iodide by metallic sodium at temperatures above 800° , the reverse reaction occurring; near the melting point of the iodide, calcium is displaced by sodium. Hence sodium is more electropositive than calcium at low temperatures, but less so at high ones. At 800° , potassium is still more positive than calcium, but it is less positive than strontium, whilst at low temperatures it is almost certainly more so.

T. E.

Solubility of Calcium Sulphate in Solutions of Other Salts. FRANK K. CAMERON and B. E. BROWN (*J. Physical Chem.*, 1905, 9, 210—215).—The solubility of calcium sulphate in solutions of ammonium chloride and of ammonium nitrate was determined. In the first case, the solubility rises with increasing concentration of the ammonium chloride until a maximum is reached at about 210 grams of ammonium chloride per litre, when the calcium sulphate dissolved is 10.9 grams per litre, the temperature being 25° . With a further increase in the ammonium chloride, the solubility of the calcium sulphate decreases. In the case of ammonium nitrate solutions, a maximum solubility of about 12.2 grams per litre is reached for a solution containing about 750 grams of ammonium nitrate per litre. The solubility at 25° in saturated solutions of sodium chloride, sodium

nitrate, sodium sulphate, magnesium chloride, and magnesium nitrate was also determined, the values, in grams per litre, being respectively 5.52, 7.16, 2.58, 1.09, 15.26. The great difference between the concentrations in the saturated solution of the two magnesium salts is very remarkable (see Abstr., 1904, ii, 544).
L. M. J.

Hydration and Hardening. PAUL ROHLAND (*Zeit. Elektrochem.*, 1905, 11, 129—130).—A reply to Jordis (this vol., ii, 155). The author insists that the hardening of cement cannot be explained by the hydration and other chemical changes alone, since these changes are sometimes not accompanied by hardening.
T. E.

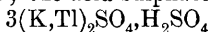
Boiler Deposits. J. M. ROTHSTEIN (*Zeit. angew. Chem.*, 1905, 18, 540—545).—The paper includes a number of analyses of boiler deposits and of the waters from which they were derived.
A. McK.

Spectrum of Magnesium. JAMES BARNES (*Chem. Centr.*, 1905, i, 994—995; from *Physikal. Zeit.*, 6, 148—151).—The temperature of certain stars has been deduced from the fact that magnesium lines have been found in their spectra. The presence of these lines is, however, not only dependent on temperature, but also on electrical conditions. Photographs of the magnesium spectrum, formed by means of the arc in hydrogen and air under different pressures, show that when the current is decreased the lines become fainter. Whilst the intensity of the lines of the arc-spectrum is found to be less in hydrogen than in air, the lines of the spark-spectrum have a greater intensity in hydrogen. The intensity of the line 4481 of the spark-spectrum becomes greater as the current is decreased. In the spectrum obtained by means of an arc in a vacuum, this line appears at the cathode and its intensity is constant.
E. W. W.

Electrolytic Refining of Lead in Hydrofluosilicic Acid Solutions. HANS SENN (*Zeit. Elektrochem.*, 1905, 11, 229—245).—Coherent deposits of lead or cadmium can be obtained from acid solutions of the silicofluorides, using anodes of lead or cadmium. A small addition of gelatin to the solution diminishes the tendency to form dendritic crystals at the cathode. The quality of the deposit is unfavourably affected by high current density or by dilution of the electrolyte; the best results are obtained with a solution containing about 11 per cent. of free hydrofluosilicic acid and 4—8 per cent. of lead (or 2.5 per cent. of cadmium) and 0.1 gram of gelatin per litre for lead, or 0.3 gram per litre for cadmium. The best current density at the cathode is from 0.005 to 0.01 ampere per sq. cm. The temperature is of little importance. Copper, bismuth, or antimony, when present in the anode lead, even in large quantities, remain undissolved so long as the anodic current density does not exceed about 0.01 ampere per sq. cm.

The separation of lead and platinum is impossible, a crystalline compound of lead and platinum having approximately the composition PtPb_2 remaining undissolved. In all cases, the anode mud contains silica and lead fluoride, which are produced by hydrolysis of lead silicofluoride. The current yield at the cathode is about 98 per cent. of the theoretical.
T. E.

Isomorphism of Potassium and Thallous Salts. WILLEM STORTENBEKER (*Rec. Trav. chim.*, 1905, **24**, 53—65. Compare Abstr., 1903, ii, 470).—The author has, in continuation of previous work, compared the sulphates, thionates, perchlorates, chlorates, chlorides, and nitrates of potassium and of thallium. The results of optical measurements and of analyses of series of mixed crystals, which are tabulated in the original, show that the perchlorates and neutral sulphates are isomorphous; the acid sulphates of the type



and possibly also those of the type $5(\text{K,Tl})_2\text{SO}_4 \cdot 3\text{H}_2\text{SO}_4$ are isodimorphous, and the simple salts KHSO_4 and TlHSO_4 probably isotrimorphous (compare Gossner, *Zeit. Kryst. Min.*, 1904, **39**, 381). The chlorates, nitrates, and thionates are regarded as isodimorphous (compare Abstr., 1903, ii, 470; and Roozeboom, Abstr., 1892, 266). Crystals of potassium chloride containing about 2 per cent. of thallium chloride were prepared by Lehmann's method (*Zeit. Kryst. Min.*, 1885, **10**, 335). It is pointed out that both the analogy of crystalline form and the property of forming mixed salts increase with the degree of oxidation of the salts of the two metals and seem to exist in higher degrees in the salts containing chlorine than in those containing sulphur.

T. A. H.

Electrolytic Behaviour of Copper Sulphide. GUIDO BODLÄNDER and KASIMIR S. IDASZEWSKI (*Zeit. Elektrochem.*, 1905, **11**, 161—182).—The experiments described were made in porcelain tubes or crucibles heated in an electrical muffle furnace of special design. The melting point of cuprous sulphide is 1091° . When the fused sulphide is electrolysed with carbon electrodes, the current is proportional to the applied *E.M.F.*; there is no decomposition point and no polarisation, and after the electrolysis no copper is found at the cathode. By fusing cuprous sulphide and copper together, it is found that copper dissolves in the fused sulphide and crystallises out on cooling, the separation beginning at a point a little above the melting point of the sulphide; in the solid state, they do not mix at all. The conductivity of solid cuprous sulphide is also studied, and Hittorf's statements (*Ann. Phys. Chem.*, 1851, **84**) confirmed. Cuprous sulphide, when fused and cast in sticks, has a comparatively small resistance in the cold; when remelted with metallic copper several times, its resistance increases enormously. When a sample of the substance having a high resistance is electrolysed at 113° , a polarisation is observed, and metallic copper was found at the cathode; at the ordinary temperature, there is no polarisation and no decomposition. The phenomena may be explained thus: pure cuprous sulphide, at the ordinary temperature, is practically a non-conductor; the conductivity observed is due to the presence of varying quantities of cupric sulphide, which is a very good conductor. At about 110° , some change occurs in cuprous sulphide (accompanied by heat absorption), owing to which it becomes an electrolyte. The electrolysis, however, produces cupric sulphide at the anode, and so the electrolytic conductivity of the cuprous sulphide soon becomes insignificant compared with the metallic conductivity of cupric sulphide. The resistance of solid cuprous sulphide diminishes

very rapidly as the temperature rises; electrolysis was observed up to 1000° . The partial decomposition of fused cuprous sulphide into copper and cupric sulphide explains the negative result of the electrolysis of the fused substance.

Potassium sulphide (previously fused in a carbon crucible in order to eliminate oxygen compounds) was electrolysed at about 300° , and sodium sulphide at about 650° . A decomposition point, at which potassium or sodium is formed, was found in both cases at about 1.6 volts, but considerable currents pass at lower *E.M.F.*s owing to the presence of potassium or sodium hydrogen sulphide. Fused sodium and cuprous sulphides are mutually soluble to a limited extent. They combine partially to form the compound NaCuS , which remains in the form of steel-blue needles when the solid mass is treated with water. When a fused mixture of sodium sulphide and cuprous sulphide is electrolysed, copper migrates to the anode in the form of a complex anion, whilst a little copper is reduced at the cathode owing to the secondary action of the sodium formed there. T. E.

Action of Mercuric Iodide on Sulphuric Acid and Mercury Sulphates. ALFRED DITTE (*Compt. rend.*, 1905, 140, 1162—1167. Compare Abstr., 1879, 299; 1880, 12).—The compound $\text{HgI}_2, 3\text{HgSO}_4$ is readily obtained in the form of white, silky needles by heating mercuric iodide with Nordhausen sulphuric acid, or less readily when pure sulphuric acid is used; it can be recrystallised from sulphuric acid, melts to a yellow liquid which solidifies on cooling to a white, fibrous mass, and is decomposed by water, forming mercuric iodide and the tribasic mercury sulphate, $3\text{HgO}, 2\text{SO}_3$.

By the prolonged action of saturated solutions of mercuric sulphate in sulphuric acid of different strengths on mercuric iodide, five different double salts of mercuric sulphate and iodide can be obtained, the compound $\text{HgI}_2, 4\text{HgSO}_4$ crystallising with 15 or $18\text{H}_2\text{O}$ from a 41.1 per cent. solution of sulphuric acid; the compound

$\text{HgI}_2, (2\text{SO}_3, 3\text{HgO}), (\text{SO}_3, \text{HgO}), 10\text{H}_2\text{O}$ in brilliant, white needles from a 37.5 per cent. solution of sulphuric acid; the compound $\text{HgI}_2, 2(2\text{SO}_3, 3\text{HgO}), 10\text{H}_2\text{O}$ in white, nodular, crystalline masses from a 28.5 per cent. solution of sulphuric acid; the compound $2\text{HgI}_2, 3(2\text{SO}_3, 3\text{HgO}), 10\text{H}_2\text{O}$ in rose-coloured crystals from a 16.6 per cent. solution of sulphuric acid; and the compound $\text{HgI}_2, (2\text{SO}_3, 3\text{HgO})$ in white crystals from a 9 per cent. solution of sulphuric acid. M. A. W.

Preparation of Anhydrous Chlorides of the Rare Metals. CAMILLE MATIGNON (*Compt. rend.*, 1905, 140, 1181—1183. Compare Abstr., 1901, ii, 602; 1902, ii, 263, 505, 556; 1904, ii, 132, 340, 341; Muthmann and Stützel, Abstr., 1900, ii, 142; Moissan, Abstr., 1900, ii, 726).—The anhydrous chlorides of the rare metals can be obtained readily, and in large quantity, by the action of a mixture of chlorine, sulphur chloride, and hydrogen chloride on the solid obtained by evaporating at 134 — 140° the hydrochloric acid solution of the corresponding oxide, and the following compounds have been prepared: lanthanum chloride in colourless, transparent crystals; neodymium

chloride in clear, rose-coloured crystals; praseodymium chloride in green, transparent crystals; samarium chloride in pale yellow, transparent crystals; and yttrium chloride in colourless, transparent plates.

M. A. W.

Arc Spectrum of Scandium and its Relation to Celestial Spectra. Sir J. NORMAN LOCKYER and F. E. BAXANDALL (*Proc. Roy. Soc.*, 1905, 538—545).—A complete list is given of the scandium lines observed, those due to impurities (chiefly cerium, thorium, and ytterbium) being eliminated by comparison with the spectra of all the chemical elements available at Kensington. The number of lines in the solar spectrum which undoubtedly correspond with scandium lines is greater than the number ascribed to scandium by Rowland. The authors find that of the 23 scandium lines of intensity 6 or above, 18 occur in the solar spectrum, 3 are doubtfully present, and 2 appear to be absent. The scandium lines which occur in the chromospheric spectrum, although not so numerous as those in the solar spectrum, are of considerably greater prominence. It is quite probable that the stronger scandium lines occur also in the spectra of stars resembling the sun.

J. C. P.

Europium and its Ultra-violet Spectrum. Sir WILLIAM CROOKES (*Proc. Roy. Soc.*, 1905, 74, 550—551).—The author has photographed the spectrum of europium from the oxide prepared by Urbain (see Abstr., 1904, ii, 340). The photographs show that this europia contains gadolinium, yttrium, lanthanum, and calcium.

J. C. P.

Manganese Chromates. MAX GRÖGER (*Zeit. anorg. Chem.*, 1905, 44, 453—468).—The author has examined the precipitates obtained by the action of sodium chromate on manganous chloride under different conditions of concentration and temperature. The composition of these precipitates varies, owing to the change undergone by the manganous chromate first formed, which probably decomposes according to the equation $3\text{MnCrO}_4 = \text{Cr}_2(\text{MnO}_3)_3 + \text{CrO}_3$.

Potassium manganous chromate, $\text{K}_2\text{CrO}_4 \cdot \text{MnCrO}_4 \cdot 2\text{H}_2\text{O}$, prepared by the gradual addition of an *N*/1 solution of manganous chloride to a *4N* solution of potassium chromate, separates in reddish-brown prisms. When more dilute potassium chromate is used, the precipitate obtained is not uniform. Chromic manganite, $\text{Cr}_2\text{O}_3 \cdot 3\text{MnO}_3$, appeared to be formed in certain cases.

Different products are obtained by the action of ammonium chromate on manganous chloride according to the conditions employed.

A. McK.

Structure of Hardened Steel. W. A. KURBATOFF (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1524—1539, and 1905, 37, 169—180).—The usual reagent employed for etching polished steel surfaces to show their structure is a 5 per cent. alcoholic solution of either picric or nitric acid, by which the sorbite constituents are rendered dark, while the martensite and austenite remain pale. The author has made

experiments to discover reagents which will distinguish between martensite and austenite and bring out other details of structure.

The results obtained show that the rapidity of the action on steel of solutions of nitric or picric acid in different solvents is proportional to the degree of association of the molecule of the solvent, or the degree of electrolytic dissociation of the dissolved substance. Nitro-compounds take part in the formation of the layer conditioning the colouring, which has a complex structure. The most sensitive reagents for distinguishing the constituents of complex steels are: (1) a 4 per cent. solution of nitric acid of sp. gr. about 1.3 in *isoamyl* alcohol, and (2) a 20 per cent. solution of concentrated hydrochloric acid in *isoamyl* alcohol mixed with one-third of its volume of a saturated solution of nitroaniline in alcohol. With troostite-sorbite mixtures, the best results are obtained with either (1) a mixture in equal volumes of a 4 per cent. solution of nitric acid in acetic anhydride, methyl alcohol, ethyl alcohol, and *isoamyl* alcohol, or (2) 3 volumes of a saturated solution of nitrophenol mixed with 1 volume of a 4 per cent. solution of nitric acid in alcohol.

The hardness of austenite is not the same in all specimens and does not remain constant in any one specimen. During annealing, martensite and austenite are transformed into plates of cementite containing troostite within them, whilst above 350° troostite and cementite change into ferrite and cementite, the quantity of the last-named increasing. Austenite, martensite, troostite, and troostite-sorbite may occur in the form of identical pseudo-crystals. All possible forms of transition between troostite, sorbite, troostite-sorbite, martensite, austenite, &c., have been found to exist.

The paper is accompanied by micro-photographs.

T. H. P.

Colloidal Ferric Hydroxide. II. Influence of Ammonium Chloride. A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 213—220. Compare this vol., ii, 37).—Conductivity measurements of mixtures in various proportions of colloidal ferric hydroxide solution and ammonium chloride solution show that in these mixed solutions the ammonium chloride distributes itself between two solvents, namely, water and the molecules of the colloid. T. H. P.

Cobalt Chloride. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 7, 51. Compare Abstr., 1904, ii, 741 and 821).—The violet-coloured liquid produced by the exposure of a solution of cobalt chloride in ethylene glycol to sunlight absorbs less light than the initial red solution, the diminution being in the ratio 1:0.6. The violet solution regains its original red colour when removed from the light or when the solvent is distilled off. T. A. H.

Cobaltic [Fluoride]. GIUSEPPE BARBIERI and FILIPPO CALZOLARI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 464—465).—When a saturated solution of cobaltous fluoride in fuming hydrofluoric acid (40 per cent.) is subjected to electrolysis in a platinum dish which serves as the anode, and using a platinum wire cathode and an anode current density of about 1 ampere per sq. dm., *cobaltic fluoride*, CoF_3 , is

deposited as a green powder which does not redissolve when the current is stopped. The salt remains unchanged for several days in a desiccator, but in the air it gradually becomes grey and then red in colour. It is soluble in concentrated sulphuric acid, giving a brown solution which becomes green on dilution, whilst the addition of a few drops of water to the salt blackens it owing to the separation of cobaltic hydroxide. Its solution in sulphuric acid turns red when gently heated, or on the addition of a reducing agent such as alcohol, a nitrite, or a salt of hydroxylamine or hydrazine; hydrogen peroxide reduces the solution instantaneously.

Electrolysis of the corresponding nickel fluoride under similar conditions does not yield a nickelic fluoride. T. H. P.

Electrolytic Chromium. I. HECTOR R. CARVETH and W. ROY MOTT (*J. Physical Chem.*, 1905, 9, 231—256).—The work of previous observers is briefly reviewed and the possible reactions during electrolysis are considered. It was found that in a solution containing 100 grams of metal per litre at a temperature of about 21°, with a current density of about 50 amperes per square decimetre, the efficiency slowly increased until a constant value of about 30 per cent. was reached. The author considers this to be due to the formation of chromous chloride and that this is necessary for the efficient electrolysis. Subsequent experiments showed that the bubbling of air caused a great decrease in the efficiency. Rise of temperature may also cause a marked decrease of efficiency owing probably to the increased rate of oxidation of the chromous salt. Variation of the anode liquid was also found to cause considerable alteration in the electrolysis, and high efficiencies were obtained with ammonium hydroxide as anolyte; this effect of the anolyte is most probably due to diffusion into the cathode chamber. L. M. J.

Solid Solutions of Indifferent Gases in Uranium Oxide. VOLKMAR KOHLSCHÜTTER and K. VOGDT (*Ber.*, 1905, 38, 1419—1430).—Hydroxylamine uranate, $\text{UO}_4\text{H}_2(\text{NH}_3\text{O})_2\cdot\text{H}_2\text{O}$, prepared by the addition of hydroxylamine hydrochloride to the orange precipitate produced by alkalis in solutions of uranyl salts, forms well characterised, yellowish-green crystals. When slowly heated at 125°, it decomposes into water and ammonia, which pass away, and into nitrogen and nitrous oxide, which remain practically entirely dissolved in the uranic acid, and escape on dissolving the residue in dilute acids. Uranium oxide only exercises this power of retaining indifferent gases so long as it contains traces of water, the real solvents being hydrates of uranium trioxide. It is suggested that the water present plays an important part in the retention of such gases as helium in uranium minerals. E. F. A.

Two Double Sulphates of Uranyl. WILLIAM OECHSNER DE CONINCK and CHAUVENET (*Bull. Acad. roy. Belg.*, 1905, 7, 50. Compare Abstr., 1904, ii, 821, and this vol., ii, 254).—When a mixture of uranic hydrate with potassium hydrogen sulphate is compressed by Spring's process (Abstr., 1904, ii, 472), Ebelmen's salt, $\text{K}_2\text{SO}_4\cdot\text{UO}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$,

is obtained, and this, on recrystallisation, furnishes the more hydrated salt, $K_2SO_4 \cdot UO_2SO_4 \cdot 3H_2O$. The corresponding trihydrated form of ammonium uranyl sulphate was also obtained by crystallisation from a solution of ammonium and uranyl sulphates. T. A. H.

Cæsium Uranyl Sulphate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 7, 94. Compare preceding abstract).—This salt was prepared by crystallisation from an aqueous solution containing molecular proportions of cæsium and uranyl sulphates. It has the formula $Cs_2SO_4 \cdot UO_2SO_4 \cdot 2H_2O$. T. A. H.

Crystallisation of Tin and Zinc by the Electrolysis of their Salts. A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 153—156).—Crystallised tin may be obtained in a compact form, in which it can be readily removed from the bath and examined, in the following manner. A clean sheet of glass, resting on two pieces of glass rod in a flat photographic dish, is covered with stannous chloride solution, a piece of copper wire serving as anode and a piece of tin, at a distance of 10—15 cm., as cathode. On passing through the solution the current from a couple of accumulators, crystallised tin begins to deposit at the point of contact of the copper wire with the glass, and forms long, straight rods from which numerous branches jut out at right angles.

Crystalline zinc may be obtained in a similar way from its chloride or sulphate, the crystals obtained being, like those of tin, convenient for examination under the microscope. Photographs of the crystals of the two metals are given. T. H. P.

New Series of Isomorphous Salts. ITALO BELLUCCI and NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 457—463. Compare Miolati and Bellucci, *Abstr.*, 1900, ii, 732, and 1901, ii, 246; Bellucci, *Abstr.*, 1902, ii, 267; 1903, ii, 155, and 1904, ii, 180; Bellucci and Parravano, *Abstr.*, 1904, ii, 822 and 823, and this vol., ii, 40).—That the stannates, plumbates, and platinates are isomorphous is shown by the following crystallographic measurements of the potassium salts made by ZAMBONINI: These potassium salts all crystallise in the rhombohedral system. For potassium stannate, $Sn(OH)_6K_2$ [$a:c = 1:1.9588$; $\alpha = 70^\circ 0' 44''$]; for potassium plumbate, $Pb(OH)_6K_2$ [$a:c = 1:1.9514$; $\alpha = 70^\circ 10' 26''$]; for potassium platinate, $Pt(OH)_6K_2$ [$a:c = 1:1.9952$; $\alpha = 69^\circ 11' 4''$]. T. H. P.

Thorium. CHARLES BASKERVILLE (*Ber.*, 1905, 38, 1444).—In connection with Meyer and Gumperz' criticisms (this vol., ii, 257) of the author's work (*Abstr.*, 1902, ii, 85; 1904, ii, 663), attention is drawn to the need for carefully following the original directions.

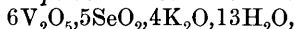
J. J. S.

Complex Compounds of Quinquevalent Vanadium with Quadrivalent Elements. WILHELM PRANDTL [with FRITZ LUSTIG] (*Ber.*, 1905, 38, 1305—1310).—*Vanadiselenious acid*, $3V_2O_5 \cdot 4SeO_2 \cdot 4H_2O$, is formed by boiling vanadium pentoxide with selenious acid in aqueous solution; on cooling, it separates as a yellowish-red, crystalline, doubly

refracting powder, consisting of small, golden leaflets, containing $6\text{H}_2\text{O}$, if obtained from a solution containing an excess of selenious acid or if evaporated with hydrochloric acid, or $10\text{H}_2\text{O}$ if prepared from equal weights of vanadium pentoxide and selenium dioxide; the water of crystallisation is driven off at 100° .

Two series of vanadiselenites are obtained: red salts, by boiling equal weights of vanadium pentoxide and selenium dioxide together in water, adding sufficient aqueous alkali hydroxide to form a clear, slightly alkaline solution, and acidifying with acetic acid; yellow salts, formed in the same manner from 1 part by weight of vanadium pentoxide with 10 parts by weight of selenium dioxide.

Red ammonium vanadiselenite, $6\text{V}_2\text{O}_5, 5\text{SeO}_2, 4(\text{NH}_4)_2\text{O}, 13\text{H}_2\text{O}$, crystallises in large, glistening, dark red, almost opaque, doubly refracting cubes, is slightly soluble in water, and decomposes when boiled with water. *Red potassium vanadiselenite*,



forms spherical aggregates of dark red crystals, or, when air-dried, a red powder consisting of doubly refracting needles.

Yellow ammonium vanadiselenite, $3\text{V}_2\text{O}_5, 6\text{SeO}_2, 3(\text{NH}_4)_2\text{O}, 2\text{H}_2\text{O}$, forms small, yellow, doubly refracting needles with parallel extinction.

Yellow potassium vanadiselenite, $3\text{V}_2\text{O}_5, 6\text{SeO}_2, 3\text{K}_2\text{O}$, forms a yellow, crystalline powder. G. Y.

Precipitation of Gold in the Crystalline Form. ROBERT DYKES (*Chem. News*, 1905, 91, 180).—Crystals of gold have been obtained from a combined solution of uranium nitrate and auric chloride in ether by concentrating, then adding water, and again concentrating, but sometimes amorphous gold forms and then the crystals are only obtained after the further addition of auric chloride to the filtered solution, followed by evaporation. Crystals of gold have also been deposited from a solution of auric chloride kept in the dark for some days in a sealed tube. The crystals are isometric and exhibit the usual properties of gold. D. A. L.

Colloidal Metals of the Platinum Series. I. ALEXANDER GUTBIER and G. HOFMEIER (*J. pr. Chem.*, 1905, [ii], 71, 358—365. Compare Abstr., 1903, ii, 81; 1904, ii, 414; this vol., ii, 24, 327).—Stable liquid hydrosols of platinum, palladium, and iridium are obtained by reduction with hydrazine hydrate of very dilute solutions of salts of these metals in presence of gum arabic. These hydrosols, after dialysis, can be filtered and concentrated to a certain extent by warming; they are stable towards light, but are decomposed when shaken with barium sulphate or animal charcoal. The solid hydrosols obtained by evaporation over sulphuric acid in a vacuum are completely soluble in warm water. G. Y.

Absorption of Oxygen by Platinum. RICHARD LUCAS (*Zeit. Elektrochem.*, 1905, 11, 182—185).—A tube of quartz was filled with platinum gauze, exhausted, and filled with pure oxygen. When the tube is heated to a constant temperature, the pressure of the oxygen diminishes. The absorption begins at 615° and increases in rapidity up

to 1000°, after which it again diminishes. The platinum gauze used contained about 5 per cent. of iridium. It was found that perfectly pure platinum does not absorb oxygen at all; the action is therefore due to the iridium. T. E.

Palladium. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1905, **38**, 1388—1394).—According to Jannasch and Bettges (*Abstr.*, 1904, ii, 519, 594), the product obtained by the reduction of palladium salts with hydrazine sulphate and subsequent ignition is a mixture of oxides. It is here shown that palladium salts are reduced to metallic palladium by hydrazine either in alkaline or in acid solution (compare *Abstr.*, 1904, ii, 180), the product obtained being entirely soluble in aqua regia. The oxide found in Jannasch's experiments is formed during the ignition of the precipitate in the air. E. F. A.

Palladium Hydride. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1905, **38**, 1394—1397).—The behaviour towards hydrogen of palladium black, prepared either by reducing the chloride with hydrogen or with hydrazine sulphate in acid or alkaline solution, was studied by heating the metal at 110° in a stream of hydrogen and subsequently keeping it at -10° in an atmosphere of hydrogen. The palladium hydride was then heated in a stream of carbon dioxide, a specially devised apparatus being employed to prevent the access of air, and the amount of hydrogen eliminated was measured. The results show that the amount of hydrogen occluded is greatly increased by cooling to -10°. Palladium hydride preparations rich in hydrogen are pyrophoric. E. F. A.

Colloidal Metals of the Platinum Group. II. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1905, **38**, 1398—1405. Compare *Abstr.*, 1904, ii, 180).—Colloidal palladium is prepared by passing a current of hydrogen through a solution of sodium protalbate and palladium chloride at 60°. After dialysis, the solution is evaporated on the water-bath and the residue dried in a vacuum. Colloidal palladium hydride may be prepared by heating the solid palladium hydrosol in a stream of hydrogen at either 60° or 110°, preferably at the higher temperature. The product loses its hydrogen when heated in carbon dioxide at 130—140°, at which temperature the sodium protalbate present in the preparation is still undecomposed. The residue of palladium still forms a colloidal solution with water. E. F. A.

Rendering Active of Hydrogen by Colloidal Palladium. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1905, **38**, 1406—1409).—Colloidal platinum, dissolved in water, brings about the conversion into aniline of nitrobenzene in alcoholic solution, through which hydrogen is passed. The amount of aniline formed varies greatly with the temperature and the amount and age of the palladium preparation used. In presence of palladium hydrogel, or of palladium black, aniline is not formed. E. F. A.

Influence of Temperature and Pressure on the Absorption and Diffusion of Hydrogen in Palladium. ADOLF WINKELMANN (*Ann. Physik*, 1905, [iv], **16**, 773—783).—A critical examination of

Schmidt's work (Abstr., 1904, ii, 312). The author considers that his earlier experiments, which led him to the assumption of the dissociation of the hydrogen molecules (Abstr., 1902, ii, 552), cannot be interpreted merely by reference to adsorption, as suggested by Schmidt.

J. C. P.

Mineralogical Chemistry.

Behaviour of Pennsylvanian Naphtha and its Products towards Polarised Light. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 221—223. Compare Abstr., 1904, i, 641, and this vol., ii, 328).—Pennsylvanian naphtha and its distillation products exhibit slight optical activity, a fact which points to the organic origin of the naphtha. The residue, non-volatile at 250° under the ordinary pressure, has a rotation three times as great as that of the original naphtha. T. H. P.

[**Martite from Mexico.**] OLIVER C. FARRINGTON (*Field Columbian Museum, Chicago, Geol. Ser.*, 1904, 2, 197—228).—In a paper on the geology and geography of the State of Durango is given a description of the Cerro Mercado, a mountain of iron-ore situated close to the city of Durango. The ore consists mainly of hæmatite, which varies considerably in character, being hard or soft, red or black, specular or earthy; cavities in the ore are usually lined with crystals of martite. These crystals are unmodified octahedra of an iron-black colour; the colour of the streak is cherry-red, and none of the powder is attracted by a magnet. A polished surface shows that the crystals are not homogeneous, there being enclosures in the form of red, triangular patches or irregular spots. The following analysis of crystals, by H. W. Nichols, shows that they consist of hæmatite, 90·12, limonite, 8·35, and pyrites, 1·29 per cent.

Fe ₂ O ₃ .	FeO.	H ₂ O.	TiO ₂ .	MgO.	SiO ₂ .	S.	Total.
97·26	0·78	1·21	trace	trace	0·25	0·69	100·19

This composition, together with the fact that magnetite is not known to occur at the locality, suggests that the martite of Cerro Mercado may be a pseudomorph after pyrites. The paper also gives several analyses of rhyolite. L. J. S.

Atopite from Brazil. EUGEN HUSSAK (*Centr. Min.*, 1905, 240—245).—Small, octahedral crystals of atopite, a mineral previously known only from the manganese mine at Långban in Sweden, have been found at Miguel Burnier in Minas Geraes. The crystals vary in colour from pale sulphur-yellow to reddish-brown; they are sometimes twinned according to the spinel law and have an imperfect octahedral cleavage. The following analysis made on sulphur-yellow crystals

agrees with the usual formula, $(\text{Ca}, \text{Na}_2, \text{Fe}, \text{Mn})_2\text{Sb}_2\text{O}_7$. The mineral contains more manganese and less iron than the Swedish atopite.

Sb_2O_5 .	CaO .	MnO .	FeO .	Na_2O .	K_2O .	Total.	Sp. gr.
76.20	12.68	5.70	trace	5.70	trace	100.28	5.1

A description is given of the modes of occurrence of the extensive deposits of manganese ores in this and in other parts of Brazil.

L. J. S.

The Mount Vernon Meteorite. WIRT TASSIN (*Proc. United States National Mus.*, 1905, 27, 213—217).—This mass, weighing 159.21 kilos., was found in Mount Vernon township, Christian Co., Kentucky, about thirty-five years ago, but its meteoric origin has only recently been recognised. It is of the pallasite type, consisting of a reticulated mass of nickel-iron (33.12 per cent. of the whole), in which are embedded rounded blebs of olivine (63.15 per cent.) with varying amounts of troilite (0.69 per cent.), schreibersite (1.95 per cent.), carbon (0.09 per cent.), chromite (1.00 per cent.), and lawrencite. The various constituents have the compositions given below: I, nickel-iron; II, taenite; III, schreibersite; IV, troilite; V, a specular material, essentially a graphitic iron, lining the olivine cavities; VI, chromite; VII, olivine.

	Fe.	Ni.	Co.	Cu.	S.	SiO_2 .	Al_2O_3 .	C.	P.	Cl.
I.	82.52	14.04	0.95	0.10	0.29	0.81	0.41	0.46	0.39	trace
II.	63.99	35.98	0.10	trace	—	—	—	—	0.04	—
III.	64.99	18.90	0.10	trace	—	—	—	—	15.70	—
IV.	62.99	0.79	—	—	36.35	—	—	—	trace	—
V.	84.90	5.04	—	—	1.75	2.99	0.94	2.81	1.47	0.10
	SiO_2 .	MgO .	FeO .	Fe_2O_3 .	Al_2O_3 .	Cr_2O_3 .	Mn.	NiO.	P.	
VI.	1.38	4.96	17.97	—	9.85	64.91	—	—	—	—
VII.	35.70	42.02	20.79	0.18	0.42	—	0.14	0.21	trace	—

L. J. S.

Mount Dyrring, Barraba, and Cowra Meteorites. JOHN C. H. MINGAYE (*Rec. Geol. Survey, New South Wales*, 1904, 7, 305—307).—The meteorite found at Mount Dyrring, in the Singleton District, New South Wales, weighed 25 lbs. and is of the pallasite type. It consists of nodules of pale green, vitreous olivine (forming 72 per cent. of the mass), enveloped by magnetic iron in an advanced state of rust; the latter represents nickel-iron (25 per cent.), but there is now no metallic portion. Analysis gave the results under I (also traces of MnO , K_2O , CoO , TiO_2 , CuO , Au , Pt , Ir , Pd ; tin and vanadium are absent).

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	CaO .	MgO .	Na_2O .	NiO .	Cr_2O_3 .
I.	25.64	1.32	29.90	7.65	0.01	27.90	0.14	2.11	0.11
	SO_3 .	CO_2 .	P_2O_5 .	Cl.	H_2O (at 100°).	H_2O (>100°).	Total.	Sp. gr.	
I.	0.15	0.13	0.51	0.01	0.82	3.89	100.29	5.411	

The Barraba meteoric iron has the composition given under II. On dissolving the iron in hydrochloric acid, bright metallic needles and

laths shred from the mass; as shown by analyses III and IV, this material is not uniform in composition, and it consists largely of a mixture of schreibersite and rhabdite together with kamacite.

	Fe.	Ni.	Co.	Cu.	Sn.	Pt, Ir.	Mn.
II.	93.50	5.54	0.51	0.01	0.02	traces	trace
III.	62.27	21.69	0.46	—	trace	trace Pt	—
IV.	64.12	[24.60]		—	—	—	—
V.	85.26	13.23	1.02	0.02	trace	—	trace
VI.	51.45	34.10	trace	—	—	—	—

	P.	S.	Si.	C.	Total.	Sp. gr.
II.	0.27	nil	0.01	0.03	99.89	7.761
III.	15.53	—	—	—	99.95	6.339
IV.	11.28	—	—	—	100.00	—
V.	0.22	0.01	0.01	0.02	99.79	7.805
VI.	13.09	—	—	—	99.49*	—

* Insol. 0.85.

The Cowra meteoric iron gave the results under V, and the schreibersite isolated from it those under VI.

L. J. S.

Physiological Chemistry.

Antagonism of Salts. JACQUES LOEB (*Pflüger's Archiv*, 1905, 107, 252—262).—Freshly fertilised *Fundulus* eggs develop in distilled water or in sea water, but rapidly die in a pure solution of sodium chloride of equivalent strength. If to this salt solution a small amount of a salt of a bivalent metal is added, development goes on. Even poisonous salts such as barium chloride or zinc sulphate will do; they neutralise the toxicity of sodium chloride, and sodium chloride antagonises their poisonous action. It therefore appears that if both salts are present, their diffusion into the egg is slower than when only one is in solution. There is a similar antagonism between certain bivalent metallic salts; for instance, between magnesium chloride and the chlorides of calcium, strontium, and barium. The poisonous action of sodium chloride can also be neutralised by the addition of the chlorides of calcium and potassium, although not by one of them alone. This is probably true for all sea animals. W. D. H.

Regulation of Lung Ventilation. JOHN S. HALDANE and J. G. PRIESTLEY (*J. Physiol.*, 1905, 32, 225—266).—Normal alveolar air can be obtained in man by a simple method, the principle of which is to collect a sample of expired air at the end of inspiration and the end of expiration; the mean of the two gives the composition of alveolar air. At constant atmospheric pressure, it contains a nearly constant percentage of carbon dioxide in the same person; in different individuals, this percentage varies. With varying atmospheric pressures, the per-

centage varies inversely as the atmospheric pressure, so that the carbon dioxide pressure remains constant, whilst the oxygen pressure varies widely; this no longer holds when the oxygen pressure in the air falls below 13 per cent. of an atmosphere.

The respiratory centre is very sensitive to any rise in the alveolar carbon dioxide pressure, a rise of 0.2 per cent. being sufficient to double the amount of alveolar ventilation during rest. When the oxygen pressure in the inspired air falls below about 13 per cent. of an atmosphere, the respiratory centre begins to be excited by want of oxygen, and the alveolar carbon dioxide pressure begins to fall; but in more ordinary circumstances it is the carbon dioxide pressure in the arterial blood (which will vary with that in the alveolar air) which determines the activity of the respiratory centre. During work, for instance, the alveolar carbon dioxide pressure goes up slightly, and the lung ventilation is consequently much increased. Determinations of the tidal air in a number of people by a method in which the whole body except the head is placed in a plethysmograph gave numbers much in excess of those found by Hutchinson, and later by Marcet, being 500 c.c. or more. The respiratory "dead space" is about 30 per cent. of this. The amount of air breathed per minute and per unit of body weight during rest varies widely in the same individual, and still more widely in different individuals.

Apnoea depends on a fall of the carbon dioxide pressure in the respiratory centre to below the threshold exciting value, the oxygen pressure being at the same time sufficiently high not to excite the centre. If the inspired air contains enough carbon dioxide to prevent the fall below this threshold, even a short apnoea cannot be produced. In man under normal conditions it is therefore unnecessary to assume the existence of a true vagus apnoea.

W. D. H.

Investigations on the Circulation in Man. ADOLF LOEWY and H. VON SCHRÖTTER (*Chem. Centr.*, 1905, i, 1172—1173; from *Zeit. exp. Path. Ther.*, 1, 197—311).—The following conclusions relate to man. The elasticity of the lung tissue is so complete that withdrawal of the air from closed portions does not alter their volume. Such closure does not alter the amount of oxygen in the blood; in the closed alveoli, the tension of the gases approaches that in venous blood (oxygen 5.3, carbon dioxide 6, and nitrogen 89 per cent.). The venous blood is 60—65 per cent. saturated with oxygen; about 34 per cent. of the arterial oxygen is used by the tissues, that is, 6.5 c.c. per 100 litres of blood. A number of interesting figures relating to the amount of blood are given, and to the work of the heart. The duration of a complete circulation is given as 72 seconds; the output of each heart beat 55 c.c., or 1/84 of the total blood volume; the daily work of the heart 10,000 metre-kilograms, or 3.6 per cent. of the day's energy. At least 139 c.c. of blood pass the coronary circulation per minute, or about 7 times as much as in the rest of the resting parts of the body.

W. D. H.

Contractility of Intracranial Vessels. WILHELM WIECHOWSKI (*Chem. Centr.*, 1905, i, 1040; *Arch. exp. Path. Pharm.*, 52, 389—428).—In anæmic, but not in normal animals, antipyrin increases the tone of

the intracranial blood-vessels. Certain analgesics appear to act on the heat-regulatory centre as well as on the vasomotor centre which controls the intracranial vessels; both centres are placed in the *corpus striatum*.
W. D. H.

Spectroscopy of Normal Blood and of Crystalline Oxy-hæmoglobin. A. VILA and M. PIETTRE (*Bull. Soc. chim.*, 1905, [iii], 33, 505—510. Compare this vol., i, 399).—By using tubes from 10 to 50 cm. long in place of the glass dishes of small dimensions usually employed in spectroscopic observations of blood, the authors have observed, in addition to the two well-known bands in the green, the existence of an absorption band ($\lambda = 634$) in the red, with solutions of fresh blood in distilled water, and also with dilute aqueous solutions of various specimens of oxyhæmoglobin prepared from the blood of different animals. In the case of oxyhæmoglobin from the blood of the guinea-pig, the same absorption band was also shown by a preparation of the crystals. This absorption band appears to be identical with that generally associated with the presence of methæmoglobin, which has so far been supposed to occur only in blood which has undergone change. With preparations of blood suspended in isotonic solutions, only the two bands in the green were observed. It is possible, therefore, that the red absorption band becomes associated with the colouring matter only when it has escaped from the corpuscle.
T. A. H.

Effect of Acids upon Blood. C. E. HAM and HERMANN BALEAU (*J. Physiol.*, 1905, 32, 312—318).—In the conversion of oxyhæmoglobin into acid hæmatin by the action of acids, half the amount of replaceable oxygen, as obtained by the ferricyanide method, is liberated. Methæmoglobin is not an intermediate stage in the conversion. Other proteins can replace globin in the oxyhæmoglobin molecule. If ammonium sulphide is added to hæmin prepared by Schalféeff's method, hæmochromogen is formed; if globin or egg-white is added, hæmoglobin is regenerated. The action of acid is to resolve the combination between oxygen and globin, and to combine with the globin, forming acid albumin and liberating free oxygen. On this hypothesis, oxyhæmoglobin has the formula $O:\text{Fe}(\text{C}_{16}\text{H}_{15}\text{ON})_2\cdot\text{O}\cdot\text{G}$, where G represents the globin group. The two oxygen atoms are linked to iron, but not in the same way, one being more firmly united. This is what one would expect from its chemical behaviour towards strong and weak acids.
W. D. H.

Effect of Phosphorus on the Coagulation of Blood. Origin of Fibrinogen. MAURICE DOYON, ALBERT MOREL, and N. KAREFF (*Compt. rend.*, 1905, 140, 800—801).—Poisoning by phosphorised oil produces in dogs fatty degeneration of the liver, the disappearance of fibrinogen from the blood-plasma, and incoagulability of the blood. In the cock, these effects do not occur. The loss in fibrinogen varies with the intensity of the fatty degeneration; the changes in the blood are secondary to those in the liver.
W. D. H.

Reduction of Oxyhæmoglobin. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1905, 140, 993—995).—Anæmia, anæsthetics, and microbial infections, especially with *Staphylococcus*, increase the time required for the reduction of the oxyhæmoglobin of the blood with ferrous sulphate to twice or thrice the normal. The observations were made on dogs and men.

W. D. H.

Natural Nourishment of Infants. MAX RUBNER and OTTO HEUBNER (*Chem. Centr.*, 1905, i, 1172; from *Zeit. exp. Path. Ther.*, 1, 1—25).—A metabolism research on a boy 5½ months old. On mother's milk (1.99 grams nitrogen, of which 1.63 was of proteid origin, 37.7 grams fat, and 80.5 lactose per diem), it put on daily, on the average, 0.46 gram of nitrogen. The carbon intake was insufficient, but in spite of this the child increased in weight at the rate of 83 grams a day, of which the nitrogen only accounted for 10 grams, allowing for the loss of carbon; water in the main accounted for the remainder. Of the total energy, the proteid in the diet accounted for 5 per cent. The small amount of proteid necessary is noteworthy. The child was extraordinarily active and cried much. Important conclusions are deduced concerning infants' diet, and nutrition in general. In different children, from 91 to 94 per cent. of mothers' milk is utilised.

W. D. H.

Behaviour of Salt Solutions in the Stomach. ERNST OTTO (*Chem. Centr.*, 1905, i, 1037; from *Arch. exp. Path. Pharm.*, 52, 370—388).—Whether the stomach plays the part of a protective organ against the introduction of saline solutions of varying strength into the intestine, was investigated on dogs with duodenal fistula. Its action in this direction is quite unimportant. In fact hypotonic or hypertonic solutions are never rendered isotonic, the solutions passing far too rapidly through the stomach.

W. D. H.

Concentration of Hydrogen Ions in Pure Gastric Juice, and its Relation to Electrical Conductivity and Acidity. The Influence of the Alkaline Earths on the Reaction of Animal Fluids. PAUL FRAENCKEL (*Chem. Centr.*, 1905, i, 1171; from *Zeit. exp. Path. Ther.*, 1, 431—438, 439—445).—The concentration of hydrogen ions in the gastric juice obtained from dogs by Pawloff's method is measured by the electrical method. It varies within comparatively narrow limits around 0.1*N*. It is raised by injection of pilocarpine. The amount of hydrochloric acid approaches that obtained by titration with Congo red as indicator. The juice always contains proteid. Examination of gastric juice from children led to the same results.

A small increase in hydrogen ions is produced by neutral salts of the alkaline earths.

W. D. H.

Influence of Different Proteids, Asparagine, and Lecithin in Nitrogenous Metabolism. W. VÖLTZ (*Pflüger's Archiv*, 1905, 107, 360—415, 415—425).—The nitrogen of paranuclein is better absorbed than that of serum albumin, but the latter substance leads to a greater putting on of nitrogen in the body. Asparagine is not

entirely absorbed, but some is found in the fæces; it is of little value in itself in producing an increase of proteid in the body. If it is given with paranuclein, the proteid metabolism is much increased; in the case of casein and asparagine, this is markedly so; the increase is less when asparagine is given with serum albumin. Proteid metabolism is favoured by the administration of lecithin; this is attributed to the phosphorised constituent of the molecule. In the same individual on the same diet, considerable variations in proteid metabolism are noticeable.

W. D. H.

The Pancreas and Glycolysis. RICHARD CLAUS and GUSTAV EMBDEN (*Beitr. chem. Physiol. Path.*, 1905, 6, 343—348. Compare Abstr., 1904, ii, 179).—A second polemical paper against Cohnheim.

W. D. H.

Spleen and Pancreas. II. OSCAR PRYM (*Pflüger's Archiv*, 1905, 107, 599—620).—The theory originated by Schiff and supported, among others, by Herzen and Bellamy, that the spleen forms some substance necessary for the transformation of the pancreatic trypsinogen into trypsin, receives no support from the present experiments carried out with infusions of the two organs. A favourable result on pancreatic activity does often follow admixture with spleen infusion, but this is no specific influence of the spleen; it is due to dilution and to bacterial activity, the boric acid used by Herzen as an antiseptic not being an efficient one.

W. D. H.

Proteolytic Products of the Splenic Enzyme acting in an Alkaline Medium. E. PROVAN CATHCART (*J. Physiol.*, 1905, 32, 299—304).—The proteolytic enzyme in the spleen (*lieno- β -protease*), which acts in an acid medium, has been investigated by Leathes (Abstr., 1902, ii, 615). The present research relates to *lieno- α -protease*, the enzyme active in an alkaline medium. The following products were isolated: histidine, inactive arginine, lysine, tyrosine, leucine, alanine, aminovaleric acid, pyrrolidine-2-carboxylic acid, glutamic acid, phenylalanine, and ammonia. Aspartic acid was probably also present. Tryptophan was not isolated, although there was a well-marked glyoxylic reaction. The main differences from what Leathes found are (1) the nature of the arginine (Leathes found the optically active variety); (2) the proportion of aspartic and glutamic acids (Leathes found more of the former).

W. D. H.

Proteid Decomposition and Acidosis in Extreme Hunger. THEODOR BRUGSCH (*Chem. Centr.*, 1905, i, 1173—1174; from *Zeit. exp. Path. Ther.*, 1, 419—430).—The observations were made on Succi, the fasting man. The fast lasted 31 days; during the last 10 days there were signs of acidosis. The urea output was lessened, that of ammonia increased; the urine contained considerable quantities of β -hydroxybutyric acid; this, with acetoacetic acid and acetone, is considered to originate from the fat of the body, for in a woman in a reduced condition owing to an œsophageal tumour, there was no trace of acidosis.

The purine substances tend to fall to a value below that found during a purine-free diet. The phosphoric acid excretion indicates that more muscular proteid and less bone substance disintegrate than in earlier researches and in other fasting men. W. D. H.

Differences in Staining Reaction of Living and Dead Protoplasm. VLADISLAV RŮŽIČKA (*Pflüger's Archiv*, 1905, 107, 497—534).—Mosso has introduced a differential stain for dead and living protoplasm, and Rhumbler uses the same reagent, methyl-green. In the present research, a mixture of neutral-red and methylene-blue is recommended, and full histological instructions are given for its use. As a result of numerous observations on various kinds of cells, animal and vegetable, it is proved that the staining with red is a sign of life, with the blue a sign of death. Some theoretical deductions concerning the nature of the reaction are entered into, the main outcome of which is that two different reducing groups exist in the protoplasm, but it is admitted that no complete explanation can be forthcoming until more is known of the chemistry of protoplasm. W. D. H.

Basophil Granules in Nerve. J. S. MACDONALD (*Proc. Physiol. Soc.*, 1905, xxxvii—xxxviii; *J. Physiol.*, 32).—In nerve fibres stained by "neutral red," minute, stained granules are thickly deposited in the vicinity of an injury, and coarse granules develop in the neighbouring portion of the axis cylinder at irregular intervals of its length, but at intervals of time proportional to the distances between the granules. In cooled frogs, these granules are yellow, and some disappear. In warmed frogs, they are red and more permanent. The cooled nerve fibre thus appears to be alkaline, the warmed acid. This may be interpreted as (1) distinction between active and resting nerve; but attempts to change the reaction by stimulation have failed; (2) as due to the different reaction of the muscles from among which the nerve was removed; or (3) as due to a change in the partition of acids and bases owing to the difference in temperature. The granules are either a precipitation of the dye, stained coagula of proteid, or a combination of the two. The appearances are similar to those depicted by Macallum in his microchemical test for potassium salts (this vol., ii, 270). By his method, potassium salts may be detected wherever the axis cylinder is injured, which otherwise escape detection. At an injured spot, the axis cylinder seems to separate into a central coagulated albuminous core, and an outer solution of salts. The injury current can only be explained as a consequence of diffusion at the site of injury; this could be reduced, balanced, or reversed by alterations in the medium into which diffusion occurs; but the solutions necessary to balance the injury were found to be so extraordinarily concentrated as to diminish the trust to be placed on the significance of the fact. The microscopical evidence now adduced shows that a salt solution of great concentration is found at the injured spot. Should such evidence bear critical examination, important conclusions may be drawn as to the chemical constitution of the axis cylinder. W. D. H.

Alcohol and Acetone in the Tissues and Fluids of the Body. F. MAIGNON (*Compt. rend.*, 1905, 140, 1063—1065, 1124—1126).—Small quantities of alcohol and acetone were found in all the tissues and in the blood and urine. These are produced during life. They are oxidised with the formation first of acetic acid, and finally carbon dioxide and water. They are considered to originate from dextrose.

W. D. H.

Acetone-formation in the Body. II. GIUSEPPE SATTA (*Beitr. chem. Physiol. Path.*, 1905, 6, 376—391).—The research relates to substances which act inhibitably on acetone formation; they were found to be galactose, laevulose, glycerol, tartaric acid, lactic acid, and citric acid; malonic acid does not act in this way. A discussion on the explanation of these results follows. Acetone-formation is believed to occur in the organs not in the alimentary tract.

W. D. H.

Variations in Dextrose, Glycogen, Fat, and Albumin in the Course of the Metamorphoses in the Silk-worm. C. VANEY and F. MAIGNON (*Compt. rend.*, 1905, 140, 1192—1195).—The variations in sugar, glycogen, fat, and albumin in the course of the metamorphoses of the silk-worm are given; for instance, during silk formation there is a great increase in albumin and glycogen.

W. D. H.

Animal Lactase. H. BIERRY (*Compt. rend.*, 1905, 140, 1122. Compare Abstr., 1904, i, 840).—Negative attempts to confirm the conclusions of Weinland (Abstr., 1900, ii, 93; 1901, ii, 30) and of Bainbridge (Abstr., 1904, ii, 424).

W. D. H.

Philo-catalase and Anti-catalase in Animal Tissues. FR. BATTELLI and MLE. L. STERN (*Compt. rend.*, 1905, 140, 1197—1198. Compare Abstr., 1904, ii, 499).—Anti-catalase is the name given to a "ferment" capable of destroying catalase in the presence of oxygen. It occurs in many tissues, such as spleen, liver, and lung. In several tissues and in the blood serum there exists still another substance having the properties of a ferment and possessing the power of destroying anti-catalase, thus protecting catalase; it is named philo-catalase.

W. D. H.

Acid Dyscrasia. ALEXANDRE DESGREZ and MLE. BL. GUENDE (*Compt. rend.*, 1905, 140, 882—884. Compare Abstr., 1904, ii, 193).—From experiments on guinea-pigs, in which the urine was examined after administration of various aromatic acids, the following conclusions are drawn. The elaboration of proteid matter is diminished under the influence of the dyscrasia produced by phenylpropionic acid and its analogues. This occurs under the influence both of the saturated acids and of acids containing an acetylenic linking. The amount of phosphoric acid in the urine indicates a preponderating destruction of the phosphorylated proteins in cellular nuclei. When the molecule has not all its carbon atoms saturated, the result differs according as one uses an ethylenic or acetylenic union. The double union in cinnamic acid

exercises a favourable influence, hindering the destruction produced by the carboxylic compound, probably by giving origin to ethylenic oxide in the metabolic process. The cells of the organism preserve for a considerable time the new vital modality impressed on them by acid dyscrasia.

W. D. H.

The Distribution of Nitrogen in the Urine. GIUSEPPE SATTA (*Beitr. chem. Physiol. Path.*, 1905, 6, 358—375).—In normal individuals taking no carbohydrate, the ammonia and purine nitrogen is increased at the expense of the other substances which are precipitable by phosphotungstic acid. In diabetes, there is always an increase in the monoamino-acid fraction; ammonia is increased, whilst the urea is correspondingly diminished. In a dog without a pancreas, the urea excretion remains normal, but the monoamino-acids increase.

W. D. H.

Precipitins and Anti-precipitins. P. BERMBACH (*Pflüger's Archiv*, 1905, 107, 621—625, 626—629).—A number of observations are given regarding the amount of serum containing precipitin which is necessary to cause precipitation in various normal sera, but it is admitted that the observations are too scanty for the drawing of general conclusions, except that evidence exists for the presence in some circumstances of inhibitory materials or anti-precipitins.

W. D. H.

Toxins and Anti-toxins. I. THORVALD MADSEN and L. WALBUM. II and III. THORVALD MADSEN and HIDEYO NOGUCHI. IV. THORVALD MADSEN (*Chem. Centr.*, 1905, i, 1264—1266; from *Bull. Acad. Sci. Lettres Danemark*, 1904, 425—446, 447—456, 457—464; 1905, 1—10).—I and II. *Influence of Temperature on the Reaction Velocity.*—Arrhenius' formula for the influence of temperature on reaction velocity does not hold for the hæmolysis produced by alkalis; the constant diminishes with time, and at low temperatures = 0. The law, however, holds for various forms of agglutination, in certain cases with some variations for the action of acids on red corpuscles, but not for the action of lecithin.

III. *Saponin-cholesterol.*—The action of saponin on the corpuscles is believed to depend on the combination it forms with cholesterol; this is borne out by an examination of the dissociation curve of the compound.

IV. *The Poison of Botulism and its Antitoxin.*—As in some other cases where there is no direct relation between quantity and action, the neutralisation point is difficult to determine.

W. D. H.

Action of Calcium Permanganate on Tetanic and Diphtheritic Toxins and on Tuberculin. J. BAUDRAN (*Compt. rend.*, 1905, 140, 884—886).—Calcium permanganate not only destroys the toxicity of alkaloids such as strychnine, but also that of tetanus toxin, diphtheria toxin, and tuberculin. The products obtained all contain calcium and manganese.

W. D. H.

Absorption of Chloroform in Later Stages of Anæsthesia. BERTRAM J. COLLINGWOOD (*Proc. Physiol. Soc.*, 1905, xxviii—xxx; *J. Physiol.*, 32).—In the early stages of anæsthesia, large amounts of chloroform are absorbed. After a long period of anæsthesia, the dosage of the drug being kept constant, the amount absorbed is not great. When the organism is fully saturated with the narcotic, a very low percentage is necessary to maintain anæsthesia. The numbers given relate to cats. An improved form of tonometer for the estimation of chloroform is figured and described. W. D. H.

Poisonous Symptoms in Dogs with Eck's Fistula. C. J. ROTHBERGER and HEINRICH WINTERBERG (*Chem. Centr.*, 1905, i, 1175; from *Zeit. exp. Path. Ther.*, 1, 312—359).—The workers of the St. Petersburg school state that dogs with an Eck's fistula exhibit toxic signs when meat, carbamic acid, ammonia, and glycine are given. In the present research, no such results were obtained; the dogs stand a meat diet well. They are easily poisoned by strychnine given by the mouth or subcutaneously, but are more resistant to tolylenediamine than normal dogs, thus resembling dogs in which the spleen has been extirpated. W. D. H.

Chemistry of Malignant Growths. III. Nucleo-histon as a Constituent of Tumours. S. P. BEEBE (*Amer. J. Physiol.*, 1905, 13, 341—349).—A good method of separating nucleo-histon from nucleo-proteid is that of Huiskamp and Bang, who precipitate the former in neutral solutions by calcium chloride. Bang obtained no nucleo-histon from five fibro-sarcomas, but in a sixth case obtained a substance from a sarcoma of the testis with the characters of lymph-gland nucleo-histon. Nucleo-histon was not found in normal testis. In the present research, fourteen tumours were examined, but the only undoubted cases in which nucleo-histon was found were in the lymph-glands. A difficulty of the investigation is the occurrence of degenerations in tumours, and nucleo-histon is easily changed by autolysis into a condition which gives no precipitate with calcium chloride. The general conclusion drawn is that nucleo-histon is not a common constituent of tumours. Neuberg's work on the occurrence of pentose in cancer is regarded as important and suggestive. W. D. H.

Action of Formic Acid on Tremors. E. CLÉMENT (*Compt. rend.*, 1905, 140, 1198—1199. Compare Abstr., 1904, ii, 430).—The increase of muscular tonus said to be the result of the administration of formic acid led to its being given for tremors. It was given to a woman aged sixty-five who had trembled for ten years, and to a man aged seventy-two who had trembled for eighteen years. The result was amelioration of the condition. W. D. H.

Treatment of Trypanosomiasis. A. LAVERAN (*Compt. rend.*, 1905, 140, 1081—1084. Compare this vol., ii, 272).—Further details are given of the treatment of *Trypanosoma gambiense* infections by arsenious acid and trypan-red. The present research gives an account of two monkeys cured by this method. They had been infected with

the parasite from a case of sleeping sickness. Three or four alternate doses, with 8 or 10 days' intervals, of arsenious acid injected subcutaneously or intravenously, and trypan-red given in sufficient quantity to redden the skin and the excretions, are sufficient. W. D. H.

Behaviour of Iodoform in the Body. PAUL MULZER (*Chem. Centr.*, 1905, i, 1174—1175; from *Zeit. exp. Path. Ther.*, 1, 446—479).—Iodoform was given by an oesophageal sound to rabbits. The iodine mainly reappears in the urine as alkali iodide and iodate; this excretion lasts for 6 or 7 days; the faeces contain only traces. About 60 per cent. of the iodine is thus found. Iodoform as such passes neither into the urine nor the expired air. Iodine is found also in the sweat and hair. The lethal dose is 1—2 grams per rabbit. It acts as a narcotic in dogs but not in rabbits. The toxic symptoms are respiratory with convulsions and paralysis; the reflexes are diminished, and towards the end the temperature sinks rapidly. Fatty degeneration is the most marked post-mortem sign. W. D. H.

Pharmacology of Ethyl Salicylate. ELIJAH M. HOUGHTON (*Amer. J. Physiol.*, 1905, 13, 331—340).—Ethyl salicylate is a colourless, volatile, slightly soluble, oily liquid with a pleasant characteristic odour and taste. It is not an antiseptic. It has little or no local irritant action. It is quickly absorbed from the stomach or subcutaneously and is rapidly excreted by the kidneys. It stimulates certain nerve centres, producing in large doses frequent respiration and a lowering of blood-pressure and cardiac activity. If pushed, the animal dies from paralysis of the respiratory centre and diastolic standstill of the heart; this is due to the direct action of the drug on the muscular tissue. Compared to the methyl compound, it is less toxic and produces less intestinal irritation. W. D. H.

Sense of Taste in Pharmacy and Pharmacology. WILHELM STERNBERG (*Chem. Centr.*, 1905, i, 1042; from *Ber. deut. Pharm. Ges.*, 15, 36—45).—The effect of chemical composition on taste has been investigated in the case of several drugs, but more especially for "dulcin" and its homologues. *p*-Phenetolecarbamide,

$\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$,
p-anisolecarbamide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, the compound,
 $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$,

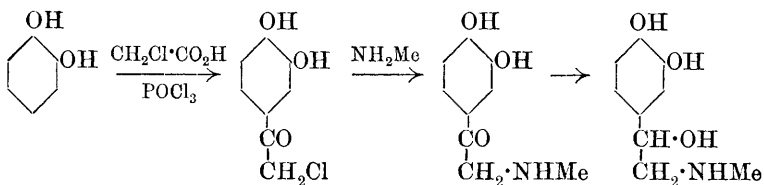
and *as*-dimethylcarbamide, $\text{NMe}_2 \cdot \text{CO} \cdot \text{NH}_2$, have a sweet taste; but *s*-dimethylcarbamide, $\text{CO}(\text{NHMe})_2$, and *s-p*-diphenetolecarbamide, $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$, are tasteless. Similarly, carbamido-*p*-phenoxyacetic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, is without taste, but the ammonium salt of tolylenedioxamic acid, $\text{C}_6\text{H}_4\text{Me}(\text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{H})_2$, is intensely sweet. E. W. W.

Action of Camphor on the Circulation. E. SELIGMANN (*Chem. Centr.*, 1905, i, 1039; from *Arch. exp. Path. Pharm.*, 52, 333—345).—Camphor in certain circumstances strengthens the heart-beat, and induces regular beats in a surviving heart which exhibits fibrillary contractions. No certain action on the vaso-motor mechanism could be determined. W. D. H.

Action of Camphor on the Frog's Heart poisoned with Chloral Hydrate. A. BÖHME (*Chem. Centr.*, 1905, i, 1039—1040; from *Arch. exp. Path. Pharm.*, 52, 346—369).—A frog's heart, rendered slow-beating or even quiescent with chloral hydrate, is rendered more active with camphor. Its use as a cardiac stimulant is recommended.

W. D. H.

Physiological Action of Synthetical Substances allied to Adrenaline. HENRY D. DAKIN (*Proc. Physiol. Soc.*, 1905, xxxiv—xxxvi; *J. Physiol.*, 32. Compare *Proc.*, 1905, 21, 154).—Starting from catechol, it is possible to prepare a base with properties similar to those of adrenaline. The stages are given in the following formulæ, the details being reserved for a later communication :



The formula of the final product, which is Jowett's for adrenaline, is given provisionally, for there are certain differences between the new base and adrenaline; for instance, the synthetical base is optically inactive; its salts, however, show all the reactions of those of adrenaline, and its physiological activity is as great; less than a millionth of a gram will raise the blood-pressure. The intermediate ketone (Friedmann's adrenalone) is not much more powerful physiologically than the chloroacetyl catechol from which it is prepared.

A number of allied substances have been prepared which may be grouped chemically as follows :

I. The simplest member of the series $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$.

II. Derivatives of the type $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHR}$.

(a) Where R is an aliphatic group.

(b) Where R is a mixed group, like benzyl.

(c) Where R is aromatic, like phenyl.

III. Derivatives of the type $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NR}_2$.

IV. Derivatives of the type $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NR}_3\cdot\text{OH}$.

Substances in classes I and IIa produce a marked rise of blood-pressure in doses of about 1 mg. per kilo. of body-weight, and on reduction yield bases with the activity approximately of adrenaline.

Class IIb stands both chemically and physiologically between these and those in class IIc. The latter cause fall of pressure, which may be followed by a slight rise. The di-alkyl bases (Class III) have a smaller action than those in class IIa; their reduction products, however, are very active. Only two members of class IV have been examined, the trimethyl compound, which is very active, and the phenyldimethyl compound, which is inactive.

Catechol itself, in doses of 2 mg. per kilo., causes a distinct rise in blood-pressure; the same is true for many of its simple derivatives and homologues, for instance, protocatechuic acid, pyrogallol, &c.

Substances in which the hydrogen of the phenol groups is replaced are inactive.
W. D. H.

Corydalis Alkaloids. JOHANNES GADAMER (*Arch. Pharm.*, 1905, 243, 147—154).—The physiological action of these alkaloids has been studied by Hans Meyer and Peters (Peters, *Inaug. Diss.*, Marburg, 1904). With the exception of corytuberine, they all produce, in frogs, a narcosis like that brought about by morphine, and have a prejudicial effect on the action of the heart. It is possible that bulbocapnine may find an application as a narcotic in vivisection and in veterinary practice, in the case of animals which are stimulated by morphine. In other respects, the alkaloids in question fall into three groups corresponding with their chemical differences (Abstr., 1902, i, 307); those of the corydaline group produce paralysis of the spinal cord; those of the corycavine group stimulate the motor centres; and those of the bulbocapnine group cause an increased reflex action, at any rate in frogs.
C. F. B.

Fibrin Ferments in Snake Venom. CHARLES J. MARTIN (*J. Physiol.*, 1905, 32, 207—215).—The venom of various snakes produces clotting in oxalate plasma, citrate plasma, fluoride plasma, magnesium sulphate plasma, hydrocele fluid, and solutions of fibrinogen. Hence the venom contains actual fibrin ferment; the ferment is not used up in the process, but the serum after clotting is still active in promoting coagulation; the ferment, however, if this is repeated often, gradually disappears from adsorption by the successive crops of fibrin. The small quantity of venom necessary to cause clotting is remarkable; the figures given show that this varies in different snake-venoms. The ferment is destroyed at 75°, and dialyses slightly. The ferments, however, are not identical. The serum of a horse immunised against one venom contains an anti-ferment against the clotting ferment in that venom, but not necessarily in other venoms. A very simple time-relationship was found in investigating the velocity of reaction, namely, that amount of ferment and coagulation tissue are inversely proportional.
W. D. H.

Spear Poison of the Cameroons. LUDWIG BRIEGER and M. KRAUSE (*Chem. Centr.*, 1905, i, 1171—1172; from *Zeit. exp. Path. Ther.*, 1, 93—97).—The spears used in elephant hunting are covered with a poison obtained from the wood of a *Strophanthus*-like tree by trituration. Fifty grams of the raw material yielded about 4 grams of a pure crystalline poison. This is a heart poison, resembling digitalin, and appears to be identical with strophantin.
W. D. H.

The Munchi-arrow Poison. ALFRED FRÖHLICH (*J. Physiol.*, 1905, 32, 319—326).—The poison was obtained from arrows from Northern Nigeria. The toxic principle belongs probably to the class of resinous acids. No alkaloid reaction could be obtained, no crystals formed, and the poison, unlike nearly all alkaloids, was insoluble in water. The symptoms are mainly paralytic, the heart being affected before the

skeletal muscles. *Rigor mortis* sets in early. This points to an action of the poison on the muscle proteids, but the attempts made to determine the nature of the alteration gave no positive results.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Decomposition of Calcium Cyanamide. F. LÖHNIS (*Centr. Bakt. Par.*, 1905, ii, 14, 389—400).—Experiments with twelve micro-organisms showed that nearly all of them, especially *Bacterium Kirchneri*, *B. lipsiense*, *Bacillus megatherium*, and *B. vulgare* var. *Zopfii*, liberate ammonia from calcium cyanamide at the ordinary temperature. Aëration had no essential effect on the process. Of the various organisms employed, only *B. Kirchneri* has the power of producing ammonia from urea.

Urobacillus Leubei and *Planosarcina ureæ* both liberate ammonia from calcium cyanamide; *Urobacillus Pasteuri* had very little effect.

N. H. J. M.

Influence of Different Sugar Solutions on the Temperatures at which Various Yeasts are killed. F. W. TULLO (*Chem. Centr.*, 1905, i, 1176—1177; from *Woch. Brauerei*, 22, 155—160).—The temperature at which yeast is killed was found to be 55° (for 5 minutes) in solutions of dextrose, lævulose, galactose, rhamnose, maltose, lactose, and sucrose, and in water alone. In experiments made somewhat below the maximum temperature, it was found that when heated for a long time, fermentable sugars are on the whole more unfavourable than non-fermentable sugars and water alone.

N. H. J. M.

Heliotropism indirectly caused by Radium. HANS MOLISCH (*Chem. Centr.*, 1905, i, 1033—1034; from *Ber. deut. bot. Ges.*, 23, 2—8. Compare Dixon and Wigham, *Sci. Proc. Roy. Dublin Soc.*, 10, ii, No. 19, and Koernicke, *Ber. deut. bot. Ges.*, 22, 155).—Experiments on various plants have shown that although a radium preparation alone does not cause heliotropism, a mixture of a radium salt with zinc blende is very active in this respect. The effect must therefore be due to the light emitted by the phosphorescent blende and not to the radium rays. The seedlings require to be placed within 2—3 cm. of the tube containing the blende. The fact that whilst the experiments with lentils, peas, and vetches succeeded in the laboratory, similar experiments in a forcing house failed, is attributed to the presence of traces of coal gas and other impurities in the air of the former. These traces of poison affect the sensitiveness of the plant in such a way that the effect of gravity is modified or counteracted whilst the sensitiveness of the plant to light is not affected.

E. W. W.

Desiccation of Plants and Vegetable Tissues. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1905, [viii], 4, 488—490, 490—505, 506—519, 520—538, 538—552).—This series of papers gives in greater detail results already published (this vol., ii, 50—51, 111).

T. A. H.

Influence of Different Amounts of Soil on the Development of Plants. OTTO LEMMERMANN (*J. Landw.*, 1905, 53, 173—177. Compare Abstr., 1904, ii, 76).—The conclusion is drawn that it is not the space at the disposal of plants grown in pots which causes diminished growth, but the nutritive conditions due to the volume of soil, the amount of water being frequently the most important factor.

N. H. J. M.

Effects of Ammonium Salts on the Assimilation of Phosphoric Acid by Higher Plants. DMITRI N. PRIANISCHNIKOFF (*Chem. Centr.*, 1905, i, 1045; from *Ber. deut. bot. Ges.*, 22, 8—17. Compare Abstr., 1902, ii, 169).—Substitution of sodium nitrate for calcium nitrate increased the alkalinity at the end of the experiment and in some cases (buckwheat) diminished the yield. With ammonium nitrate, the reaction was neutral; with ammonium sulphate, distinctly acid. The action of crude phosphates is increased by ammonium nitrate, but diminished by ammonium sulphate.

N. H. J. M.

Composition of Lemon Juice. ADOLF BEYTHIEN and PAUL BOHRISCH (*Zeit. Nahr. Genussm.*, 1905, 9, 449—464).—The results of the analyses of about 70 samples of lemon juice are given in tabular form, the quantities of extract, citric acid, invert sugar, ash, alkalinity of ash, nitrogen, phosphoric acid, and alcohol in the various juices being recorded.

W. P. S.

The Exudation of Resins. ALEXANDER TSCHIRCH (*Arch. Pharm.*, 1905, 243, 81—98. Compare Moeller, *Zeit. allg. österr. Apoth.-Ver.*, 1896, 34).—By wounding a number of trees, both gymnosperms and angiosperms, it has been shown that the primary exudation of resin from secretory vessels, when such are present, is never large in amount; to this source, mastic, sandarac, and Strasburg turpentine are due. After a while, a much more copious secondary exudation sets in, and lasts for some time, until the wound is closed over. Under the stimulus of the wound, a formation of pathological new wood takes place, and it is in this that the resin canals are formed.

C. F. B.

Arrow Poison of the Lukarets. A. SAPIN (*J. Pharm. Chim.*, 1905, [vi], 397—398).—The dried poison contains 47 per cent. of a pure resin, 41 per cent. of vegetable debris, and 12 per cent. of ash. It appears to be the sap of *Euphorbium*.

G. D. L.

Seedling Diseases of Sugar-beet and Mangolds. LORENZ HILTNER and L. PETERS (*Chem. Centr.*, 1905, i, 1043—1044; from *Arb. biol. Abt. k. Ges. Amt.*, iv, 3; and *Zeit. Ver. Rübenzuckerind.*, 1905, 165—169).—In pot experiments, it was found that treatment with

copper, calcium, and mercuric chloride preparations was suitable in the case of unhealthy soils, but not much effect was observed in field experiments. In view of the importance of oxalates and similar compounds in connection with the occurrence of disease, it seems probable that treatment of the seed with calcium carbonate may be of use.

N. H. J. M.

Deli Tobacco. D. J. HISSINK (*J. Landw.*, 1905, 53, 135—172).—Results of manurial experiments with tobacco made at Deli (Sumatra). Analyses of the ash and determinations of the nitrogen in different forms are given.

N. H. J. M.

Feeding with Calcium Phosphate. MAX PASSON (*J. Landw.*, 1905, 53, 115—134. Compare Abstr., 1903, ii, 240, and this vol., ii, 265).—Addition of calcium phosphate to food is desirable in the case of potatoes and other foods poor in calcium phosphate and acid foods, or foods having an acid ash.

Feeding cows with calcium phosphate results in milk somewhat richer in phosphoric acid, and therefore better for calves. When given to cows about to calve, it has no effect on the bone development of the calf.

Deficiency of calcium phosphate in fodder may occur in dry summers when the plants may be unable to take up sufficient phosphoric acid from the soil. In such cases, calcium phosphate should be added in good time to the food. Precipitated calcium phosphate is the most suitable preparation. Other earthy phosphates are unsuitable.

N. H. J. M.

Analytical Chemistry.

The Question of Uniform Standardising Substances for Volumetric Solutions. S. P. L. SÖRENSEN (*Zeit. anal. Chem.*, 1905, **44**, 141—155).—This question has been the subject of discussion at the last three International Congresses for Applied Chemistry, with the special object of establishing normal methods to be adopted in disputable cases. The opinions expressed on this matter have been extremely discordant. The author directs attention to the difference between the selection of an appropriate substance for a standard, which choice has only to be made once for all, and the examination of the particular specimen of that substance, as regards its purity, and especially its freedom from adventitious moisture, which has to be undertaken every time it is employed. He rejects entirely the view put forward by Wagner that the attainment of concordant results when using two or more standardising substances for the same solution is a proof of the correctness of those results, and depends rather on the careful qualitative examination of the selected substance in circumstances which ensure a certainty as to the quantitative limit to

the sensitiveness of the tests, and he insists on the necessity of these tests being of sufficient delicacy to render negligible any errors which might result from their failure to detect impurities. M. J. S.

Use of Sodium Carbonate and Sodium Oxalate as the Standard Substances in Acidimetry. S. P. L. SÖRENSEN and A. C. ANDERSEN (*Zeit. anal. Chem.*, 1905, 44, 156—184).—In the course of researches undertaken for the 5th International Congress for Applied Chemistry, Lunge concluded that sodium carbonate is to be preferred to all other substances for standardising an acid. Whilst placing second in order of merit the author's special anhydrous sodium oxalate (Abstr., 1903, ii, 684, 750), which he found to give results 1 per mille higher than those with the carbonate, he rejects it on account of the greater skill requisite for its use. The authors show that, provided the oxalate is decomposed by the heat of a spirit flame (to exclude sulphur), no special care is necessary to obtain absolutely concordant results. They find that at no temperature is it possible to dry sodium carbonate completely without a loss of carbon dioxide, but that provided the amount of sodium hydroxide in a sample is estimated, and the corresponding loss of weight allowed for, the results agree with those given by the oxalate much more closely than was found by Lunge. Since Lunge preferred methyl-orange to phenolphthalein, the author has instituted a special comparison of the results yielded by the two indicators, and finds that in a solution feebly acid to phenolphthalein and free from carbonic acid, methyl-orange gives a yellow colour, and that a noteworthy addition of acid is necessary to obtain the transition tint, but that if, instead of adding acid, the yellow solution is saturated with carbon dioxide, the colour changes to a bright red, and an addition of alkali is required to produce the transition tint. Methyl-orange, therefore, does not in any case give the same result as phenolphthalein, and since it is not indifferent to carbonic acid its use presents no advantages where accurate work is wanted.

M. J. S.

Sodium Hydrogen Carbonate in Iodometry. WILLIAM A. PUCKNER (*Chem. Centr.*, 1905, i, 1186—1187; from *Amer. Pharm. Gesell.*, 1905, 1—9).—The author calls attention to the fact that under certain conditions iodine acts on sodium hydrogen carbonate and that in consequence an error may be introduced into iodometric analyses.

If, however, the solution contains less than 1 gram of sodium hydrogen carbonate in 100 c.c. and is also charged with carbon dioxide, no iodine will be absorbed. L. DE K.

Detection of Hydrogen Peroxide in Milk. FRANZ UTZ (*Milchw. Zentr.*, 1905, 1, 175—178).—Hydrogen peroxide can be detected in milk which has been boiled before being preserved for a much longer time than in raw milk, the enzymes in the latter quickly destroying the peroxide. Temperature also has a considerable influence on the rapidity of the disappearance of the hydrogen peroxide. Milk containing 2 per cent. of a 3 per cent. hydrogen peroxide solution, after being kept at a temperature of 12—15° for 4 hours, still gives a strong

reaction with the titanous and vanadic acid tests (Abstr., 1903, ii, 449), whilst milk containing the same quantity of peroxide, when kept at a temperature of 37.5° , ceases to give a reaction after 3 hours.

W. P. S.

Neumann's Method of estimating Chlorides. W. LEGGE SYMES (*J. Physiol.*, 1905, 32, 221—224).—With some modifications, Neumann's method is found to be convenient and accurate when direct titration is difficult, as in the blood. With appropriate adjustment of the acid mixture, neither hydrocyanic nor nitrous acid is found in the distillate. The distillate, being colourless, can be titrated directly.

W. D. H.

Estimation of Perchlorates and Chlorates in Saltpetre. D. TSCHERNOBÉEFF (*Chem. Zeit.*, 1905, 29, 442—443).—A favourable criticism of Lemaitre's process for the estimation of perchlorates in nitre (Abstr., 1904, ii, 587) and also of Hendrixson's process for the estimation of chlorates in the presence of perchlorates (Abstr., 1904, ii, 679).

L. DE K.

Reduction of Chlorates, Bromates, and Iodates with a view to the Estimation of the Halogens. PAUL JANNASCH and A. JAHN (*Ber.*, 1905, 38, 1576—1589. Compare Schlötter, Abstr., 1904, ii, 146, 167; Roberto and Roncali, Abstr., 1904, ii, 773).—Details are given of the estimation of chlorine, bromine, and iodine in chlorates, bromates, and iodates by reduction with various reagents and precipitation with silver nitrate. Potassium chlorate and bromate are reduced quantitatively by concentrated nitric acid at 275° under pressure, by fuming nitric acid at the laboratory temperature or under cooling, or by hydrogen peroxide in dilute nitric acid solution. The iodate must be heated with fuming nitric acid and silver nitrate under pressure at 340° . Potassium bromate and iodate are reduced by formic acid or by hydrazine sulphate in alkaline solution; in acid solution, the latter reagent forms azoimide. Potassium chlorate is reduced when heated with dextrose and acetic acid at 200° under pressure, but only incompletely by acetaldehyde. Hydroxylamine sulphate or acetate is the most convenient reagent for the quantitative reduction of chlorates in dilute nitric acid, or of bromates or iodates in alkaline solution.

G. Y.

Detection of Bromine in the presence of much Iodine. H. CORMIMBEUF (*Ann. Chim. anal.*, 1905, 10, 145—146).—Soluble iodides, after having been neutralised if necessary, are mixed with excess of ferric chloride, which precipitates the iodine as a black powder, which is then removed by filtration. The little iodine still in solution is boiled off and the iron is precipitated by aqueous sodium hydroxide. The filtrate is carefully neutralised with dilute sulphuric acid, a crystal of potassium chlorate and a little chloroform are added, and then a few drops of strong sulphuric acid. This liberates any bromine, which dissolves with its characteristic colour in the chloroform. Free iodine is first converted into an iodide by digestion with water and an excess of reduced iron,

L. DE K.

Free Iodine in Alkaline Solutions. CHARLES M. VAN DEVENTER (*Chem. Centr.*, 1905, i, 990; from *Chem. Weekblad*, 2, 135—137. Compare Péchard, *Abstr.*, 1899, ii, 593).—The quantity of free iodine in alkaline liquors has been determined by comparing the colour imparted to chloroform with that similarly obtained from a known quantity of iodine dissolved in a solution of potassium iodide. When a solution of 0.32 mg. of iodine and 1 gram of potassium iodide is shaken with 12 c.c. of chloroform, the latter is just perceptibly coloured. Péchard's minimum has been found to be much too high; 0.5 gram of iodine dissolved in a solution of 0.4 of potassium hydroxide in 12 c.c. contained about 1 mg. of free iodine. E. W. W.

Iodic Acid as an Oxidising Reagent. ERWIN RUPP (*Arch. Pharm.*, 1905, 243, [ii], 98—104).—The author has attempted to utilise the energetic oxidising power of iodic acid for the volumetric estimation of arsenious acid and potassium thiocyanate. The iodine liberated on adding a mixture of potassium iodate and sulphuric acid was expelled by warming, and the amount of unaltered iodic acid estimated as usual. Owing, however, to secondary reactions, the results were a failure.

In the case of formic acid, no secondary reactions occur. The action is, however, very slow, and must be assisted by heating for some time on the water-bath in a closed flask. L. DE K.

Separation of Hydrofluoric and Sulphuric Acids. RICHARD EHRENFELD (*Chem. Zeit.*, 1905, 29, 440—442).—The method is briefly as follows. The two acids are converted as usual into barium salts and weighed. The mixture is then treated for an hour with a standard solution of calcium dichromate and some hydrochloric acid; this dissolves the fluoride and leaves the sulphate, which may then be weighed by way of control. The filtrate is rendered ammoniacal, which causes a separation of barium chromate, and the excess of chromate is then estimated iodometrically. The difference in chromate represents the barium fluoride. L. DE K.

Preparation of Standard Solutions of Sulphuric Acid. BARKER NORTH and W. BLAKEY (*J. Soc. Chem. Ind.*, 1905, 24, 395—397).—For standardising solutions of sulphuric acid, the authors use pure sodium hydrogen carbonate. The latter is prepared by washing ordinary sodium hydrogen carbonate with water until free from chlorides. It is then dried on porous plates at the ordinary temperature, and afterwards powdered and placed in a moist atmosphere of carbon dioxide for several hours. When free from normal carbonate, the salt is dried over sulphuric acid or in a vacuum over phosphoric oxide. Normal carbonate cannot be detected in the dry product. The use of sodium hydrogen carbonate thus prepared gives results closely agreeing with those obtained by the gravimetric (barium sulphate) method, but about 2 per cent. higher than the results yielded by Marshall's method of determining the strength of the acid from its specific gravity. W. P. S.

Volumetric Estimation of Ammonium Salts with Sodium Hypobromite. ERWIN RUPP and E. RÖSSLER (*Arch. Pharm.*, 1905, 243, 104—114).—According to Mohr, the indirect titration of ammonium salts with sodium hypobromite gives untrustworthy results. The authors state that it is quite possible to obtain correct results by avoiding excess of alkali. They operate as follows: about 0.05 gram of the ammonium salt, dissolved in 10 c.c. of water, is slowly poured into a hypobromite solution diluted to 50—70 c.c. The amount of hypobromite should be such that about one-half or one-third should remain undecomposed. After 5—10 minutes, another 50 c.c. of water are added, then a sufficiency of dilute hydrochloric acid, and then at once potassium iodide. After two minutes, the liberated iodine is titrated with starch as indicator. In a successful test, the titrated liquid should not turn blue again for a few minutes. When dealing with free ammonia, this should be carefully neutralised.

The bromine solution must be made by dissolving 10 grams of sodium hydroxide in 500 c.c. of water and adding 17 grams of bromine. It must be standardised in the usual way with potassium iodide and is fairly permanent.

L. DE K.

Gravimetric Estimation of Nitric Acid by means of Nitron [1:4-Diphenyl-3:5-endoanilodihydrotriazole]. ALEXANDER GUTBIER (*Zeit. angew. Chem.*, 1905, 18, 494—499).—An investigation of Busch's "nitron" process (this vol., i, 307; ii, 282). Eighty c.c. of the nitrate solution containing about 0.15 gram of the nitrate are mixed with 12 drops of dilute sulphuric acid and heated to boiling, when 12—15 c.c. of a 10 per cent. solution of nitron in 5 per cent. acetic acid are added. When cold, the beaker is placed in iced water, and after an hour the precipitate is collected at the pump on a weighed Neubauer platinum crucible, and then washed with 10 c.c. of water, using 1 c.c. at a time. After drying at 105—110°, the precipitate is weighed. One part of nitron-nitrate = 0.1653 part of NO_3 . The process is recommended for the assay of commercial nitrates.

L. DE K.

Estimation of Nitric Acid in Water. MAX BUSCH (*Zeit. Nahr. Genussm.*, 1905, 9, 464—468).—One hundred c.c. of the water are heated nearly to boiling, and 10 drops of dilute sulphuric acid and 10—12 c.c. of 10 per cent. "nitron" acetate (Abstr., 1905, ii, 282) solution are added. The mixture is then placed in ice-water for 2 hours, and the crystals which form are afterwards collected on a tared asbestos filter. Any crystals remaining in the precipitation vessel are rinsed on to the filter with a portion of the filtrate. The filter and crystals are washed with 3 or 4 small quantities of ice-water, using not more than 10 c.c. altogether, dried at 105° for 1 hour, and weighed. The weight of the crystals multiplied by 0.168 gives the quantity of nitric acid (HNO_3) present.

A preliminary test may be made by treating 5 c.c. of the water with 1 drop of dilute sulphuric acid and 6 drops of the "nitron" solution. Should no crystals be obtained within 1 hour, the water contains less than 0.025 gram of nitric acid per litre. The reagent is best prepared

by dissolving the base in 5 per cent. acetic acid, warming the solution, and filtering off any insoluble matter.

W. P. S.

Titration of Phosphoric Acid. OTTOKAR J. HLAVNICKA (*Zeit. angew. Chem.*, 1905, **18**, 655—656).—A reply to Raschig (this vol., ii, 284). The author uses a slightly different process originated by Hundeshagen. The magnesium precipitate obtained in due course is washed on a hardened filter with a 2·5 per cent. solution of ammonia, and then with alcohol until free from alkali. It is removed from the filter by means of a wash-bottle, using about 200 c.c. of water, and titrated in a porcelain dish by first adding an excess of 3/10*N* hydrochloric acid, and then working back with 3/10*N* sodium hydroxide. Five drops of a solution of methyl-orange (1 : 1000) serve as indicator. One c.c. of the acid = 0·01065 gram of P_2O_5 , or 0·0060 gram of MgO .

L. DE K.

Pemberton's Method for the Estimation of Phosphoric Acid. D. J. HISSINK and H. VAN DER WAERDEN (*Chem. Centr.*, 1905, i, 1188—1189; from *Chem. Weekbl.*, 1905, **2**, 179—184).—This method is applied by the authors to the estimation of phosphoric acid soluble in water in manures as follows: 20 grams of the sample are shaken with 900 c.c. of water for 30 minutes and diluted to 1 litre. To 5 c.c. of the filtrate are added 10 c.c. of nitric acid, 15 c.c. of ammonium nitrate solution, and 25 c.c. of water containing 25 mg. of sulphuric acid. The precipitate obtained on treating this solution with Pemberton's molybdate reagent (10+5) has the composition $(NH_4)_3PO_4 \cdot 12 \cdot 65 MoO_3$, and is neutralised by 24·3 mols. of sodium hydroxide.

L. DE K.

Estimation of Phosphoric Acid in Thomas Slag. F. WESTHAUSSER (*Zeit. anal. Chem.*, 1905, **44**, 187—191).—Certain varieties of basic slag give too high a result for the citrate-soluble phosphoric acid in consequence of the solution containing silicic acid, which passes into the magnesium precipitate. Several methods have been proposed for overcoming this difficulty (compare Böttcher, *Abstr.*, 1904, ii, 148). The author has made comparative estimations with four of these methods, namely, Böttcher's, Wagner's, Hallenser's, and one adopted by the (German) Association of Agricultural Experimental Stations, which consists in evaporating the citric acid extract with hydrochloric acid to a syrupy consistence for the removal of the silica. All four methods gave results agreeing passably, although Wagner's gave slightly higher numbers than the other three.

M. J. S.

Maercker-Buhring's Solution, Wagner's Magnesium Citrate Mixture, and Ferrous Citrate Magnesium Mixture. HANNO SVOBODA (*Chem. Zeit.*, 1905, **29**, 453—456).—A study of the solvent action of these three solutions on the glass vessels in which they are stored. The amount of silica dissolved by the two Wagner solutions is not, however, large enough to seriously affect the estimation of citrate-soluble phosphoric acid in basic slags (compare also *Abstr.*, 1904, ii, 147).

L. DE K.

Detection of Certain Acids [Boric and Volatile Organic]. V. CASTELLANA (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 465—467).—The author reviews the methods given for the detection of boric acid, and gives the following new method, which is based on a reaction characteristic of boric acid alone, and is able to reveal mere traces of the acid. A little of the substance, mixed with excess of potassium ethyl sulphate, is heated in a small tube closed at one end, and the first vapours which escape are ignited; if boric acid is present, the flame produced is edged with green. In the application of this method to food materials, for example, milk, the latter is first shaken to distribute any calcium borate which may have settled to the bottom, and from 5 to 10 c.c. of the liquid then evaporated to dryness; the residue is calcined with potassium nitrate and the ash tested as above.

Potassium ethyl sulphate may also be used to detect certain organic acids, such as formic, acetic, butyric, valeric, pelargonic, oxalic, benzoic, salicylic, and cinnamic acids, and also β -naphthol. The acid or, better, one of its salts is gently heated with potassium ethyl sulphate, when the characteristic odour of the ethyl ester of the acid is emitted.

T. H. P.

Estimation of Carbon and Hydrogen in Organic Compounds. FRITZ PREGL (*Ber.*, 1905, 38, 1434—1444).—The combustion furnace is so arranged as to carry two tubes side by side. The front part of each tube is placed in an air-jacket kept at 150—180°, the following part is heated by means of stationary burners, and the back portion of each by means of a burner working on a rail, along which it is moved automatically by means of clockwork. This clockwork can be so arranged that the movement of the burner under the portion of the tube where the substance to be analysed is placed occupies 15, 50, 100, or 200 minutes.

The tube is partially filled with copper-oxide-asbestos obtained by very gently heating copper-asbestos in air. This is kept in place by means of small pieces of copper gauze, 5 cm. long, placed alternately at right angles to one another. Coils of copper gauze are placed in front and behind the asbestos. Then follow a length of 6 cm. of granular lead peroxide, a plug of glass wool, the boat, and lastly the diffusion plug of hard glass. The tube should be dried before each combustion. Compounds containing nitrogen, sulphur, chlorine, and bromine can be analysed in this way, but not those containing iodine; if this element is present, silver-asbestos should be introduced into the tube.

Wenzel's modification of the Geissler potash bulbs is recommended.

There is no need to watch the experiment when the clockwork is once set in motion, provided the oxygen supply is properly regulated.

J. J. S.

Estimation of Silicon in 50 per cent. Ferro-silicon. K. (*Chem. Centr.*, 1905, i, 1190; from *Stahl u. Eisen*, 25, 334).—0.5 gram of the impalpable powder is gently fused with 6 grams of coarsely powdered potassium hydroxide for half an hour in a closed nickel crucible supported by wire gauze. The heat is then increased,

and after 20 minutes the crucible is allowed to cool and the fused mass is dissolved in hot water. The silica is then separated as usual by evaporation with hydrochloric acid, &c.

L. DE K.

Estimation of Alkalis in Silicates by L. Smith's Method. BENJAMIN M. MARGOSCHES (*Chem. Zeit.*, 1905, 29, 385).—A reply to Steinlen (this vol., ii, 349).

L. DE K.

Detection of Sodium Salts [by means of Potassium Pyroantimoniate]. J. BOUGAULT (*J. Pharm. Chim.*, 1905, 21, 437—442).—The most favourable conditions for carrying out this well-known test are given. The reagent is prepared by heating 1 gram of antimony trichloride with a mixture consisting of 10 c.c. of 33 per cent. potassium hydroxide solution and 45 c.c. of hydrogen peroxide (10 vols.). After about 5 minutes' heating, the solution is cooled and filtered. On adding 0.5 c.c. of the filtrate to a small quantity of a solution containing a sodium salt, a precipitate is obtained. The precipitation is favoured by gently heating the mixture and then cooling it. With 0.4 mg. of sodium chloride, a precipitate is obtained at once. If potassium or lithium salts are present in the sodium salt to be tested, they must be removed previously. Sulphuric acid must be removed, as must also chlorine, bromine, and iodine. The solution of the sodium salt must be neutral or alkaline in reaction and the sodium should preferably be present as tartrate.

W. P. S.

Reactions for distinguishing Calcite and Dolomite. STANISLAUS J. THUGUTT (*Centr. Min.*, 1905, 265—266).—Following on the work of Meigen (*Abstr.*, 1901, ii, 692), F. Hinden (*Verh. Naturforsch. Ges. Basel*, 1904, 15, 201) has tried the effects of solutions of ferric chloride, copper sulphate, lead acetate, and mercuric chloride on calcite and dolomite. A fragment of calcite, when placed in a 10 per cent. solution of ferric chloride, becomes coated in 1—2 minutes with a dark reddish-brown deposit of iron hydroxide, whilst dolomite remains unaltered. In the present note, it is pointed out that this reaction was used in 1887 by J. Lemberg, who also, in 1888 and 1892, devised several other micro-chemical colour reactions for distinguishing between calcite and dolomite.

L. J. S.

New Method of estimating Magnesium Carbonate in Limestone. W. F. KOPPESCHAAR (*Zeit. anal. Chem.*, 1905, 44, 184—187).—A large quantity (50 grams) of the limestone is dissolved in the smallest possible excess of hydrochloric acid, and the greater part of the calcium is precipitated by the addition of concentrated sulphuric acid. The whole of the magnesium then remains in solution with comparatively little calcium. These are separated in the filtrate by the ordinary method, but the quantity of magnesia carried down by the calcium oxalate is too small to require notice.

M. J. S.

Analysis of Bar Copper (Reply to Hampe's Criticism). ERNST MURMANN (*Zeit. anal. Chem.*, 1905, 44, 269—286. Compare *Abstr.*, 1897, ii, 346 ; 1898, ii, 353).—For the estimation of oxygen,

the author objects to the use of filings of the metal. Owing to the compressive action of the file, it is impossible to free the surface from organic matter (often unsaponifiable) by the short boiling with alkali which alone is permissible. The sample used must be in solid fragments, taken either by sawing or cutting, and must be freed from grease, &c., by chloroform. With regard to the electrolytic estimation of copper the author argues that the method does not possess the degree of accuracy claimed for it by Hampe, since the copper deposited electrolytically and the platinum on which it is deposited undoubtedly condense weighable but uncertain amounts of air and moisture. Rose's method, if the temperature of ignition is restricted to the neighbourhood of 650° , is of at least equal accuracy, but when a mixture of hydrogen sulphide with hydrogen is used, it is necessary to replace this by carbon dioxide before cooling, since at about $200-250^{\circ}$ there is a tendency to the formation of some cupric sulphide. The sublimation of arsenic and antimony from copper by heating in hydrogen is complete at a temperature below the melting point, but not when the copper is fused, as was the case in Hampe's experiments, since the diminution of the surface more than compensates for the higher temperature. Only a small fraction of the lead present sublimes out.

M. J. S.

Titration of Copper by Potassium Iodide in presence of Arsenic: a Correction. L. MOSER (*Zeit. anal. Chem.*, 1905, 44, 196. See this vol., ii, 64).—The precipitate which the author obtained on adding sodium pyrophosphate to sodium arsenate is found to have been produced by an impurity (calcium) in the specimen of arsenate used. Pure arsenate gives no precipitate with pyrophosphate. This correction, however, in no way modifies the author's method. M. J. S.

Estimation of Small Quantities of Iron. J. WALTER LEATHER (*J. Soc. Chem. Ind.*, 1905, 24, 385—387).—Quantities of iron too small to admit of the use of the ordinary methods may be determined by means of Lovibond's tintometer. The two colour reactions, the ferrocyanide and the thiocyanate, are both applicable to the purpose, but the colorations must, within certain limits, be produced in the presence of a constant relation of reagent to iron. In the case of the ferrocyanide reaction, 1 drop of concentrated hydrochloric acid and 1 drop of 10 per cent. potassium ferrocyanide solution were added to 20 c.c. of the iron solution, when 0.001 gram of ferric oxide gave a coloration equivalent to 9 blue + 1 yellow + 3 red units of the tintometer in a $\frac{1}{8}$ inch cell. The use of the red units was necessary as the blue glasses were not so blue as the ferrocyanide coloration. The thiocyanate reaction appears to be more delicate than the ferrocyanide with minute traces of iron, as little as 0.00001 gram being determined with very considerable accuracy. With this coloration, only 2 sets of glasses are required, red and yellow, 0.001 gram of iron in 20 c.c. being found equivalent to 21 red + 18 yellow units in a $\frac{1}{8}$ -inch cell. The quantity of thiocyanate to be added is 90 times the amount of iron present, or 0.09 gram of potassium thiocyanate for 0.001 gram of iron. Two

drops of saturated potassium thiocyanate solution will contain this amount. A drop of hydrochloric acid must also be added.

W. P. S.

Separation of Iron and Aluminium from Manganese, Calcium, and Magnesium in Ash Analysis. PAUL KASCHINSKY (*J. Landw.*, 1905, 53, 179—185).—Determinations by the methods of König and Tollens of calcium and phosphoric acid in solutions of hydrogen disodium phosphate to which known amounts of calcium chloride were added showed that calcium phosphate may be precipitated with the ferric phosphate in considerable quantity according to the amounts of free acetic acid and of calcium and phosphoric acid present.

N. H. J. M.

New Characteristic Reaction of Cobalt. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1905, 10, 147).—The strongly-diluted cobalt solution is mixed with a few drops of an alcoholic solution of phenyl- or β -naphthyl-thiohydantoic acid, and then with a drop of ammonia. A crimson-red coloration is at once formed. With stronger solutions, a reddish-brown precipitate is formed. If nickel is present, a little more ammonia should be added, which dissolves the grey nickel precipitate to a colourless liquid.

L. DE K.

New Iodised Compound of Osmium. EUGENIO P. ALVAREZ (*Chem. News*, 1905, 91, 172—174).—When a solution of potassium iodide strongly acidified with hydrochloric or phosphoric acid is shaken with a drop of an aqueous solution of osmium peroxide, in the course of a minute or two a green osmium hydriodide, $\text{OsI}_2 \cdot 2\text{HI}$, forms. In the presence of ether, the reaction becomes exceedingly delicate, and a few millionths of a gram of osmium may be detected by the green tint in the ethereal layer. It is also produced when the osmium solution in presence of ether and iodine, dissolved either in water, potassium iodide, or hydriodic acid, is treated with sulphurous acid. It is soluble in water and ether, but insoluble in benzene and chloroform; it turns red in the air or when treated with nitric acid, but in solution is rendered more stable by the presence of calcium or other such chloride; nitrites precipitate osmium hydroxide from the acid solution, and permanganate and dichromate solutions are reduced by it.

D. A. L.

Variations in the Rotatory Power of Oil of Turpentine. L. RABY (*Ann. Chim. anal.*, 1905, 10, 146—147).—The author submitted a sample of oil of turpentine to fractional distillation, and noticed that each of the five fractions had a rotatory power less intense than that of the original sample; it must, however, be remarked that this particular sample was acid and moist.

After a lapse of four months, the rotatory power of the first four fractions had, however, sensibly increased. It was noticed that this increase may be induced at once by addition of an equal bulk of olive oil.

L. DE K.

Estimation of Inspired and Expired Chloroform. AUGUSTUS D. WALLER and BERTRAM J. COLLINGWOOD (*Proc. Physiol. Soc.*, 1905, xxiv—xxviii; *J. Physiol.*, 32).—The estimation of chloroform in the expired air by the densimetric method is a more difficult thing than in atmospheric air. The principal corrections to be made are for carbon dioxide, respiratory quotient, aqueous vapour, temperature, and pressure. The method of dealing with each is described. In high values of chloroform absorption, the corrections are less influential than in low values. W. D. H.

Detection of Iodoform. WILLEM STORTENBEKER (*Rec. Trav. chim.*, 1905, 24, 66—68).—It is pointed out that the toxicological detection of iodoform is difficult owing to the rapidity with which this substance is transformed, probably into an iodate, in the animal economy. For its isolation, the author recommends distillation of the material with steam, care being taken that the mixture is slightly acid. If the iodoform does not crystallise out of the distillate, it is extracted with ether and the solvent allowed to evaporate spontaneously in the dark; the residue is then recrystallised from acetic acid, since the latter does not dissolve readily the fatty acids and similar matters which are usually found with the iodoform in the distillate, and examined microscopically. The red coloration given by iodoform with sodium phenoxide is unsatisfactory for the detection of the former, since chloroform and bromoform produce the same colour. T. A. H.

Estimation of Sodium Ethoxide with Menthone. CARL TUBANDT (*Annalen*, 1905, 339, 41—93).—Vorländer's method (*Abstr.*, 1903, i, 230) of estimating sodium ethoxide in the presence of the sodium salts of weak acids has been investigated more fully. Sodium ethoxide effects the inversion of *l*-menthone into *d*-menthone or *vice versa*; the velocity of the inversion of *l*-menthone was found to be proportional to the concentration of the sodium ethoxide except in very dilute solutions. The velocity is independent of the presence of neutral sodium salts, such as sodium acetate, bromide and iodide, and potassium iodide and the sodium derivative of dihydroresorcinol; neutral esters are also without influence. The presence of menthone or menthol has no effect. Addition of water or of benzene diminishes the velocity of inversion.

d-Menthone behaves in an exactly similar manner.

Vorländer and Tubandt's observations (*loc. cit.*) on the use of the inversion of menthone as a means of estimating the acid character of organic compounds and of determining the relative strength of weak acids have been extended; the alcoholysis of salts in absolute alcoholic solution has also been followed quantitatively. The relations holding for hydrolysis are found to apply to alcoholysis, the amount of the decomposed salt being proportional to the square root of the concentration of the undecomposed salt, thus $K = x^2/(1-x)V$.

The inverting action of amines and acids on *l*-menthone has also been investigated. K. J. P. O.

The Inversion of Cane Sugar in the presence of Milk Constituents. FRANCIS WATTS and H. A. TEMPANY (*Analyst*, 1905, 30, 119—123).—In the analysis of condensed milk, the authors find that the presence of some constituent of the milk exerts a marked retarding influence on the inversion of cane sugar by citric acid. Boiling for 10 minutes is insufficient, and to obtain complete inversion the boiling should be continued for at least 40 minutes. It is shown that lactose is not the retarding constituent, and also that citric acid is entirely without inverting action on lactose even after heating for 2 hours. W. P. S.

Laboratory Notes [Chloroacetic Acids and their Estimation and Separation]. JOHAN F. A. POOL (*Chem. Centr.*, 1905, i, 1005—1006; from *Pharm. Weekblad*, 42, 165—168).—The gas obtained by heating trichloroacetic acid with a solution of potassium hydroxide contains carbon monoxide.

The quantities of acetic, chloroacetic, dichloroacetic, and trichloroacetic acids in a mixture of these acids may be estimated by the following method. The solution is titrated with a normal solution of potassium hydroxide. If a = c.c. of alkali required, M_a , M_m , M_d , and M_t the molecular weights, and p , q , r , and s the weights of acetic, chloroacetic, dichloroacetic, and trichloroacetic acids respectively in a given volume of the solution, then

$$a = 1000p/M_a + 1000q/M_m + 1000r/M_d + 1000s/M_t.$$

An equal volume of the solution is boiled with an excess of potassium hydroxide solution, and the potassium carbonate, which is formed by the action of the alkali on the trichloroacetic acid, is then estimated by precipitating as barium carbonate and titrating with a normal solution of acid. If b = c.c. of acid required, then $b = 2000s/M_t$.

An equal volume of the solution of the acids is boiled with an excess of lime water. Dichloroacetic acid (4 mols.) yields calcium oxalate (2 mols.) and calcium glycolate (2 mols.). The calcium salts are separated by means of acetic acid and the calcium carbonate obtained from the oxalate is weighed. If c = weight of calcium carbonate, then $c = 100(1000r/2M_d)$.

Finally an equal volume of the mixture of acids is boiled with potassium hydroxide solution in a reflux apparatus and the chlorides are precipitated by silver nitrate. If d = weight of silver chloride, then $d = 143.38(1000q/M_m + 2000r/M_d + 3000s/M_t)$; p , q , r , and s may be calculated from the four equations thus obtained.

Potassium nitrite reacts with chloroacetic acid to form potassium chloroacetate and nitrous acid. The chloroacetates, however, do not behave in the same way in hot aqueous solution. The non-dissociated molecules of potassium chloroacetate react with a solution of potassium nitrite, forming methyl nitrite, potassium chloride, and potassium hydrogen carbonate, whilst in the dissociated portion the ionic reaction, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\cdot + \cdot\text{OH} = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\cdot + \text{Cl}\cdot$, occurs. The quantity of nitrite cannot therefore be estimated by determining the quantity of chlorine ions formed. The second reaction may be prevented, however, by adding a concentrated

solution of a salt with a similar ion, such as potassium sulphate or potassium nitrate. E. W. W.

Estimation of Condensed Glycuronic Acids. IX. CARL NEUBERG and WILHELM NEIMANN (*Zeit. physiol. Chem.*, 1905, **44**, 127—134. Compare Abstr., 1899, i, 933; this vol., i, 412).—Phenolglycuronic acid and its homologues are most readily estimated by heating with 1—3 per cent. solution of hydrobromic acid in presence of bromine at 100° in sealed tubes and determining the amount of saccharic acid thus formed. This is effected by converting into the basic barium salt and precipitating as normal silver salt.

Good results are not obtained with euxanthic or urochloric acid.

Phenolglycuronic acid may be estimated in urine by a similar method if the urine is precipitated with saturated barium hydroxide solution, filtered, freed from excess of baryta by means of carbon dioxide, and the clear solution evaporated to 5—8 c.c. Alkyl hydrogen sulphates do not interfere with the estimation. J. J. S.

Colorimetric Estimation of Salicylic Acid in Foodstuffs. FRED. T. HARRY and W. R. MUMMERY (*Analyst*, 1905, **30**, 124—127).—The method described is particularly applicable to the estimation of salicylic acid in foods and beverages containing tannin, and is based on the solubility of lead salicylate in alkaline solutions, lead tannate being insoluble. Fifty grams of the crushed sample (jam, fruit pulp, &c.) are placed in a 300 c.c. flask, together with a little water, and 15 to 20 c.c. of a saturated basic lead acetate solution are added. The mixture is then rendered alkaline by adding 25 c.c. of approximately *N*/1 sodium hydroxide solution, after which 15 to 20 c.c. of *N*/1 hydrochloric acid are added and the whole diluted to 300 c.c. The contents of the flask are now mixed, poured on to a filter, and 200 c.c. of the filtrate collected. The filtrate is acidified with hydrochloric acid, filtered again if necessary, and extracted three times with ether. After distilling off the ether, the residue is dissolved in alcohol, made up to 100 c.c., and the salicylic acid in it estimated colorimetrically with ferric chloride as usual. Samples containing alcohol, such as beer or wine, must be rendered slightly alkaline, the alcohol evaporated off, and then neutralised, before proceeding with the separation. W. P. S.

Solubility of Glycerides in Acetic Acid and its Application to the Analysis of Butter. L. HOTON (*Rev. intern. Falsif.*, 1905, **18**, 20—23).—Five grams of the butter or fat under examination are placed in a tube 16 mm. in diameter and provided with a tap. Ten c.c. of acetic acid of sp. gr. 1.057 are added and the whole placed in a water-bath until the contents of the tube are heated to a temperature of 60°, as shown by a thermometer inserted in the tube. The latter is then withdrawn from the water-bath and, when its contents have cooled to 35°, the lower layer is drawn off into a basin, evaporated at 70°, and weighed. The portion remaining in the tube is treated once more with 10 c.c. of acetic acid and a second residue obtained. The fatty layer is finally itself evaporated. In this way, three fractions are obtained which yield certain constants for one and the same kind

of fat. The following results were given by the three fractions—A, B, and C—obtained from various fats:

	Margarine.			Lard.			Cotton oil.			Earlnut oil.		
	W.	C.	R.	W.	C.	R.	W.	C.	R.	W.	C.	R.
Fraction A	30	72	49.8	31	63	50.5	65	52	63	42	57	59
„ B	48	74	49.5	50	67	49.7	70	54	63.2	68	67	58.8
„ C	423	80	49	420	78	49.3	360	70	59.2	395	78	56

W = weight of fraction in centigrams; C = Crismer value (Abstr., 1896, ii, 506); R = refraction at 40°.

A sample of butter having a Reichert-Meissl value of 25.3, Crismer value 51, and refraction 42.8, gave the following results:

	W.	C.
Fraction A	109	48
„ B	182	49
„ C	193	57

The author has also studied the influence of the addition of cocoanut oil to butter, and found that it only slightly alters the relation of “C” to “A,” but that the weight of the fraction “C” is considerably diminished.

W. P. S.

Estimation of Moisture and Free Alkali in Soaps. KARL BRAUN (*Zeit. angew. Chem.*, 1905, 18, 573—574).—A suitable quantity of the cut-up soap is weighed into an Erlenmeyer flask of about 125 c.c. capacity and then dried in a water oven to constant weight. During the drying, the flask is fitted with a caoutchouc cork through which passes a rather wide, doubly-bent tube filled with soda-lime, which prevents the entrance of any carbon dioxide and also materially assists the drying process.

The residue is then dissolved in as little alcohol as possible and the free alkali titrated with standard acid, using phenolphthalein as indicator.

L. DE K.

The Presence of Cotton-seed Oil in Lards from Hogs fed on Cotton-seed Meal. A. D. EMMETT and HARRY S. GRINDLEY (*J. Amer. Chem. Soc.*, 1905, 27, 263—270).—The authors have proved by a number of experiments that when hogs are fed on cotton-seed meal a portion of the cotton-seed oil is absorbed and transmitted in its unaltered condition to the fat cells. This was proved by applying to the lard obtained the Bechi, nitric acid, and Halphen tests; also the following general tests for vegetable oils: Welman's phosphomolybdic acid reaction, Tollen's phloroglucinol reaction for pentosans, and Salkowski's chloroform-sulphuric acid test for cholesterol or phytosterol. Crystals resembling the latter substance were also obtained.

L. DE K.

Solubility of Quinine in Ammonia. Testing of Quinine Sulphate. WILLIAM DUNCAN (*Pharm. J.*, 1905, 74, 438—440).—Whilst quinine dissolves in ammoniacal solutions, the increased solubility, as compared with water alone, is more apparent than

real, and is due to supersaturation. Solutions containing 10 and 32.5 per cent. of ammonia were saturated with quinine, and after four months the amount of quinine in solution was determined. The solubility in 10 per cent. ammonia was found to be 1 in 2286, and in 32.5 per cent. ammonia 1 in 2505. Pure water dissolves (U.S.P.) 1 in 1960. Loss of quinine frequently takes place when, in estimating the alkaloid, ammonia is used to precipitate it. This is partly due to supersaturation, and also to hydrolysis of the ammonium salt when the precipitated alkaloid is being washed. The author, therefore, prefers calcium hydroxide solution as a precipitant. The quinine is at once precipitated and contains no calcium sulphate. W. P. S.

Estimation of Extract in Barleys. ALBERT REICHARD and GEORG PURUCKER (*Chem. Centr.*, 1905, ii, 904; from *Zeit. ges. Brauw.*, 28, 37—38).—Twenty-five grams of barley-flour are heated for 25 minutes on the water-bath with 100 c.c. of water, cooled to 45°, and mixed with 8 c.c. of a malt infusion made by treating 1 part of malt with 4 parts of water for 6 or 8 hours. After heating for half an hour at 45°, the solution is boiled on a sand-bath for half an hour, the evaporated water being constantly replaced by boiling water. After cooling to 45—50°, another 2 c.c. of malt infusion are added, and the whole is again gradually heated to 70°, at which temperature it is kept for an hour. When cold, the solution is diluted to 400 c.c. and the extract calculated from the sp. gr. as usual. Allowance is, of course, made for the solids (less the coagulable proteids) introduced by the malt solution. L. DE K.

Identification of Lecithin. RIEDEL (*Chem. Centr.*, 1905, i, 772—773; from *Apoth. Zeit.*, 20, 92—93).—An alcoholic solution of lecithin gives characteristic precipitates with cadmium and platinum chlorides. On heating with excess of baryta water, lecithin is gradually converted into fatty acids, glycerophosphoric acid, and choline. On removing the excess of barium oxide with carbon dioxide, the barium salts of the fatty acids remain undissolved, whilst the other products pass into solution. On evaporating to dryness and extracting with alcohol, the choline dissolves, and may be identified by its platinichloride. The glycerophosphate may be oxidised with nitric acid and the phosphoric acid identified by ammonium molybdate. The barium salts of the fatty acids may be decomposed by heating with dilute hydrochloric acid and the fatty acids extracted with ether. On agitating with dilute sodium hydroxide, the acids may be removed, and any cholesterol or phytosterol recovered from the solution. The amount of lecithin may be calculated from the quantity of phosphorus found, as 100 parts of lecithin = 3.94 parts of phosphorus (compare also this vol., i, 164). L. DE K.

General and Physical Chemistry.

Increase in the Rotatory Power of Aliphatic Compounds on Transformation into Cyclic Compounds. ALBIN HALLER and MARCEL DESFONTAINES (*Compt. rend.*, 1905, 140, 1205—1208. Compare Abstr., 1903, i, 503, 563).—Esters of 4-methyl-2-cyclopentanonecarboxylic acid were prepared by condensation from β -methyladipic esters and by treatment of the former compounds with metallic sodium and alkyl iodides a series of 4-methyl-1-alkyl-2-cyclopentaneonecarboxylic esters was prepared. From these, γ -methyl- α -alkyladipic acids were obtained by saponification. The boiling point (or freezing point), density, and rotatory power of the esters are given.

Esters of β -Methyladipic Acid.

Ester	Boiling point.	mm. pressure.	Sp. gr.	$[\alpha]_D$.
Methyl	126°	16	1·008 at 18°	3° 49'
Ethyl	138	15	1·04 „ 18	2 24
Propyl	166—167	16	0·964 „ 20	2 10
isoButyl.....	178—180	20	0·947 „ 18	2 9

Esters of 4-Methyl-2-cyclopentaneonecarboxylic Acid.

Methyl	110°	16	1·07 at 15°	+ 91° 7'
Ethyl	118	18	1·05 „ 15	78 24
Propyl	123—124	15	1·029 „ 15	64 45
isoButyl.....	145	25	0·956 „ 15	66 9

Esters of 4-Methyl-1-alkyl-2-cyclopentaneonecarboxylic Acids.

Ester.	Alkyl radicle.	Boiling point.	mm.	Sp. gr. at 15°.	$[\alpha]_D$.
Methyl	Methyl	105—106°	15	1·053	78° 58'
„	Ethyl	108—111	15	1·041	59 14
„	Propyl	138—140	22	1·02	53 3
„	Allyl	126—128	13	1·029	58 18
Ethyl	Methyl	112—113	15	1·01	70 0
„	Ethyl	124	15	1·01	51 7
„	Propyl	136—137	15	1·06	51 8
„	Allyl	139—141	18	1·01	62 16
„	isoButyl	188—190	20	0·994	30 33
Propyl	Methyl	125—128	14	0·991	50 28

γ -Methyl- α -alkyladipic Acids.

Alkyl radicle.	Melting point.	$[\alpha]_D$.
Methyl	80°	+ 4° 44'
Ethyl	97—98	13 31
Propyl.....	110	16 58
Allyl	104	27 53

The rotatory power of the acids was determined in alcoholic solution at a concentration approximately equal to 1/50 mol. per litre.

The numbers show the great influence of ring formation on the rotatory power, the values for the esters of 4-methyl-2-cyclopentanecarboxylic acid being about thirty times as great as those for the corresponding esters of β -methyladipic acid. With increasing molecular weight, the specific rotatory power diminishes. The introduction of alcohol groups in the 1-position in the 4-methylcyclopentane-2-carboxylic esters diminishes the rotatory power. The allyl derivatives have a greater rotatory power than the propyl derivatives.

H. M. D.

Cathode Luminescence of Crystals. ALFREDO POCHETTINO (*Nuovo Cimento*, 1904, [v], 8, 438—445).—Every mineral capable of becoming luminous under the influence of the cathode rays emits light of a characteristic colour, which, for minerals belonging to the same group, is independent of the natural colour of the crystal. In some minerals, for example, calcite and apatite, the colour of the cathode luminescence is identical with that of the fluorescence excited in it by ordinary light; in others, for instance, phosgenite and cerussite, it is similar; whilst in aragonite and certain others it is totally different. The duration of this luminescence after the cathode rays have ceased to act varies in different minerals, and is marked in calcite and orthoclase. The excitation of cathode luminescence is not equally easy with all minerals, and takes place very readily with scheelite, apatite, and anatase. The luminescence is not completely polarised in any of the minerals examined by the author, and with some, for example, anglesite and calcite, it exhibits no trace of polarisation. Inclination of the face to the cathodic pencil does not alter the qualitative relations of the phenomenon. The orientation of the plane of polarisation is not the same in crystals of the tetragonal and hexagonal systems. Anisotropy, artificially produced in an amorphous substance, produces a greater or less partial polarisation of its cathode luminescence, and to extinguish the polarised portion of the latter the short diagonal of the analyser must be placed parallel to the direction of tension and normal to the direction of compression. T. H. P.

Triboluminescence of Potassium Sulphate. DÉSIRÉ GERNEZ (*Compt. rend.*, 1905, 140, 1234—1236).—It has been previously observed by H. Rose and by Bandrowski (*Abstr.*, 1895, ii, 66 and 429) that when potassium and sodium sulphates are fused together in molecular proportion, the product dissolved in water and left to crystallise, the separation of the potassium sulphate crystals is accompanied by the emission of flashes of light. The author shows that if the hot solution of the fused sulphates is allowed to crystallise without being disturbed by external influences there is no emission of light, but flashes of light are at once observed if a crystal is touched with a piece of iron, silver, or platinum. The phenomenon appears, therefore, to be due to the disintegration of crystals already formed, and this disintegration can be readily brought about by the agitation of the containing vessels. The admixed sodium sulphate can be replaced by other substances without interfering with the phenomenon, and it

has been finally shown that crystals of potassium sulphate separating from pure aqueous solution also exhibit triboluminescence.

H. M. D.

Triboluminescence of Metallic Compounds. DÉSIRÉ GERNEZ (*Compt. rend.*, 1905, 140, 1337—1339. Compare this vol., ii, 365).—The author has examined crystals of 100 different substances, of which 74 were inorganic salts and the remainder metallic salts of organic acids, and finds that all emit light when rubbed in a glass vessel with a platinum rod. This property is not therefore manifested especially by organic substances (compare Tschugaëff, *Abstr.*, 1901, ii, 489).

T. A. H.

Some New Effects produced by Radium Bromide on a Photographic Plate. JOSEF PETRI (*Ann. Physik*, 1905, [iv], 16, 951—957).—Coins are placed on a covered photographic plate and exposed in a magnetic field to the action of radium bromide. The images of the coins on the developed plate exhibit outgrowths at their nearest points, and these are attributed to joint magnetic and thermo-electric action, in virtue of which the separate rays are crowded so much as to leave an impression on the plate.

J. C. P.

Influence of Radium on the Respiratory Energy of Germinating Grains. H. MICHEELS and P. DE HEEN (*Acad. Roy. Belg.*, 1905, 29—34).—The experiments of the authors indicate that the radiations emitted by radioactive compounds diminish the quantity of carbon dioxide evolved by germinating grains, that is, diminish the respiratory activity.

L. M. J.

Radioactivity of the Common Metals. AUGUSTO RIGHI (*Nuovo Cimento*, 1905, [v], 9, 53—64).—By placing an electrometer in a closed vessel containing carbon dioxide together with a disc of metal, cleaned immediately beforehand by means of glass paper, the author obtains the following values for the velocity of discharge of the electrometer in volts per hour:

Aluminium	...	23	Iron	...	22·9
Antimony	...	24·8	Lead	...	32·5
Bismuth	...	29·8	Silver	...	23
Cadmium	...	24·5	Nickel	...	22·9
Copper	...	23·1	Tin	...	24·4
Glass	...	22·4	Zinc	...	24·3

Lead exhibits a curious behaviour, the rate of discharge being 38 after a quarter of an hour, 33 after a further half an hour, and 24 after a further two hours; the maximum value can only be obtained again by cleaning the lead with glass paper.

The nature of the emanation from the metals which produces the discharge is unknown.

T. H. P.

Radioactive Properties of Air, Soil, and Water in and around Halle. RICHARD SCHENK (*Jahrb. Radioakt. Elektronik*, 1905, 2, 19—42).

A New Radioactive Element which emits Thorium Radiation. OSKAR HAHN (*Zeit. physikal. Chem.*, 1905, 51, 717—720).—In fractionating a mixture of bromides obtained from thorianite, it was found that whilst the radium accumulated in the least soluble fractions, the radioactivity of the most soluble portions also increased. Finally, a strongly active oxalate precipitate of about 10 mg. was obtained, which glows faintly in the dark and excites the platinocyanide and zinc sulphide screens in a marked fashion. If a current of air is blown through a solution of the substance and directed against a zinc sulphide screen, the illumination of the latter is somewhat similar to that observed in a parallel experiment with emanium. It is shown, however, that the substance cannot be actinium or emanium. The emanation from the substance is almost identical with that of thorium, but the substance itself is 100,000—200,000 times as active as thorium, and is supposed to contain a new radioactive element. J. C. P.

The Degradation Constant of the Emanations from Emanium and Actinium. OSKAR HAHN and OTTO SACKUR (*Ber.*, 1905, 38, 1943—1946. Compare Sackur, this vol., ii, 367).—The rates of decay of the activities of emanations from emanium and actinium have been determined. The activity of emanium emanation is reduced to one-half of its maximum value in 3.6 seconds, and the actinium emanation in 3.9 seconds.

The time taken for the degradation of the induced activity produced from emanium and actinium is the same, and the two elements are therefore probably identical. J. J. S.

Application of the Wehnelt Interrupter in the Measurement of Dielectric Constants by Nernst's Method. FRIEDRICH KRÜGER (*Zeit. physikal. Chem.*, 1905, 51, 739—740).—Hints as to the most favourable working conditions. J. C. P.

Temperature-coefficient of the Resistance of Tantalum. FRANZ STREINTZ (*Zeit. Elektrochem.*, 1905, 11, 273—274).—The temperature-coefficients of the electrical resistances of tantalum, platinum, and bismuth, with the atomic weights 183, 195, and 208, are 0.3, 0.37, and 0.45 per cent. respectively, in agreement with a rule previously noticed (*Abstr.*, 1902, ii, 595).

The atomic heat of tantalum probably varies with the temperature and cannot therefore follow the law of Dulong and Petit.

T. E.

Conductivity of Colloidal Solutions. JACQUES DUCLAUX (*Compt. rend.*, 1905, 140, 1468—1470).—Contrary to the experience of Malfitano (compare this vol., ii, 72), the author finds that the electrolytic conductivity of colloidal solutions, although small, is not negligible; a solution of Graham's ferric hydroxide containing 0.032 atom of iron per

litre and having a conductivity of 113×10^{-6} was separated by diffusion through a collodion membrane into a colourless filtrate having a conductivity of 82×10^{-6} and a residue containing all the colloidal granules and having a conductivity of 280×10^{-6} , thus the granules themselves have a conductivity value of 200×10^{-6} , and the conductivity of a colloidal solution is $1/500$ of that of a crystalloid solution of the same concentration. The corresponding ratios for solutions of copper ferrocyanide and arsenic sulphide are $1/800$ and $1/3500$ respectively.

M. A. W.

Electrical Conductivity of Solutions in Ethyl Bromide. Compounds of Dimethylpyrone with Acids. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 318—337. Compare Abstr., 1904, ii, 156).—Solutions in ethyl bromide of the compounds formed by dimethylpyrone with trichloroacetic acid (this vol., i, 77) exhibit a marked capability for conducting an electric current. The specific conductivity of the acid salt increases continuously with the concentration, a saturated solution (containing about 30 per cent. of the compound) possessing the maximum conductivity, the magnitude of which (0.001321) coincides approximately with the specific conductivity of centinormal potassium chloride solution (0.001225). Strong solutions of the acid dimethylpyrone compound must hence be placed in the class of feeble electrolytes. The specific conductivity of the normal dimethylpyrone compound in ethyl bromide reaches a maximum at a concentration of about 56 per cent., which corresponds with the composition represented by $C_7H_8O_2 \cdot CCl_3 \cdot CO_2H \cdot 2EtBr$. With both these compounds, the conductivity is diminished by the addition of dimethylpyrone, and with solutions of the acid compound the conductivity is increased by the addition of trichloroacetic acid, provided too great an excess of the acid is not present.

The author discusses the relation of these results to the constitution of dimethylpyrone and to the ionising capacity of ethyl bromide.

T. H. P.

Ionisation and the Coefficient of Magnetisation of Aqueous Solutions. GEORGES MESLIN (*Compt. rend.*, 1905, **140**, 1329—1331).—When the specific coefficients of magnetisation of copper sulphate, potassium ferrocyanide, and ferrous sulphate are calculated from observations of this constant, made with aqueous solutions of the salts, allowance being made for the water, the results are lower than those obtained by direct observation on the solid salts (*Compt. rend.*, 1905, **140**, 782) and the values decrease as the solutions become more dilute. Such differences are only shown by strongly magnetic salts, and seem to be due to a progressive decomposition (ionisation) with the formation of less magnetic substances. Similarly, the coefficient of magnetisation of mixtures of ethyl alcohol and water is not always intermediate between those of the two components; it reaches a maximum (1.045 compared with water as unity) when 4 per cent. of water has been added and then decreases, reaching the normal value for alcohol (1.030) when eight per cent. of water has been added.

Young has shown that the vapour tension of mixtures of alcohol and water shows a similar variation. T. A. H.

Free Energy and Heat Capacity. JAMES M. BELL (*J. Physical Chem.*, 1905, 9, 381—391).—Richards has suggested the existence of a linear relation between the temperature-coefficients of total energy and of free energy which may be written $d\Delta E/d\theta = k.d\Delta F/d\theta$ (Abstr., 1903, ii, 132). This has also formed the subject of a paper by Trevor (this vol., ii, 372). In a mathematical paper, the author comes to the conclusion that the inferences of Richards are based on insufficient experimental data, and that the existence of the linear relation just stated does not accord with experimental data and is, moreover, at variance with certain tacit assumptions in Richards' own papers.

L. M. J.

Exact Expression for the So-called Molecular Change of Critical Temperature. JOHANNES J. VAN LAAR (*Chem. Centr.*, 1905, i, 1355; from *Chem. Weekblad*, 2, 223—229. Compare Centnerszwer, Abstr., 1904, ii, 158).—The equation $1/T_1.(dT_x/dx)_0 = 2\sqrt{\Theta\phi} - (1 + \phi)$, in which $\Theta = T_2/T_1$ or the relationship of the critical temperatures of the components and $\phi = b_2/b_1$, is an exact expression for the change of temperature T_x at the lowest critical temperature of the components. Only when Θ is less than $(1 - \phi)^2$ does the change of T_x become negative. When $x = 1$, that is, on the side of the highest critical temperature, then the change of T_x is always positive and is expressed by the equation $1/T_2.(dT_x/dx)_{x=1} = (1 + \phi) - 2\sqrt{\Theta'\phi'}$, in which $\Theta' = T_1/T_2$ and $\phi' = b_1/b_2$.

Centnerszwer's results for sulphur dioxide agree with these equations when it is assumed that the liquefied gas has the molecular formula $(\text{SO}_2)_2$. E. W. W.

Experimental Demonstrations of Thermal Phenomena developed in Phosphorescent Substances; Validity of Physical Theories. P. DE HEEN (*Acad. Roy. Belg.*, 1905, 22—28).—If one of the bulbs of a Leslie's thermoscope is covered with lamp-black and the other with chalk, the former absorbs more heat than the latter, and when exposed to either solar radiation or radiation from an incandescent lamp, the liquid on the lamp-black side sinks and this condition remains permanent. If, however, the lamp-black be replaced by a phosphorescent substance of about the same absorptive power as chalk and exposed to solar radiation, then, although at first the same phenomenon takes place, yet the condition is not permanent, and after about a quarter of an hour the levels again attain equality. If then exposed to radiation of great wave-length, the reverse effect takes place, but again eventually zero is attained. The author explains these facts by the supposition that for small wave-lengths a number of ions are emitted from the atom and constitute around it a sort of phosphorescent atmosphere, whilst greater wave-lengths determine the re-entrance of the phosphorescent ions into the atom. The author discusses the impossibility of finality in physical theories and hypotheses, and, briefly, the bearing of these facts on his previous

atomic conceptions (Abstr., 1904, ii, 553). The most important idea in the new conception of molecular dynamics appears to be that which attributes the energy to the gyrational and not the translational velocity (Abstr., 1904, ii, 553).
L. M. J.

Fusibility of Mixtures of Antimony Sulphide with Cuprous Sulphide and Mercuric Sulphide. HENRI PÉLABON (*Compt. rend.*, 1905, 140, 1389—1392. Compare Abstr., 1904, ii, 42).—The freezing point of fused antimony sulphide (555°) is uniformly lowered on addition of increasing quantities of cuprous sulphide, until at 498° a eutectic point is reached, the fused mass at this temperature containing 11.0 per cent. of cuprous sulphide. On further addition of cuprous sulphide, the freezing point rises regularly at first, but the phenomena of solidification assume a somewhat complicated character when the proportion of cuprous sulphide is considerable. The process of solidification in the case of mixtures containing more than two molecules of cuprous sulphide per molecule of antimony sulphide begins at a temperature which is higher the greater the proportion of cuprous sulphide present, but in all cases the temperature at which solidification is complete is 570° , provided the molecular ratio of cuprous sulphide to antimony sulphide does not exceed ten. The observations are rendered difficult in consequence of supercooling phenomena.

The freezing point curve for mixtures of antimony and mercuric sulphides consists of two simple branches melting at a eutectic point at 455° . The eutectic mixture contains 34 per cent. of mercuric sulphide. On account of the volatilisation of the mercuric sulphide, it was not possible to study the behaviour of mixtures containing more than 68 per cent. of it. The molecular lowering of the freezing point is calculated from the data. Extrapolating to zero concentration, the data for cuprous sulphide give 797, those for mercuric sulphide give 788 (compare Guinchant and Chrétien, Abstr., 1904, ii, 538).

H. M. D.

Relative Value of the Calorimetric Methods used in the Determination of the Heat of Combustion of Volatile Organic Substances. JULIUS THOMSEN (*Zeit. physikal. Chem.*, 1905, 51, 657—672).—The methods used in determining the heat of combustion of organic substances are practically two in number. One of these is the author's, in which provision is made for the normal and regular combustion of the substance (as gas or vapour) in oxygen under the ordinary pressure; the other is Berthelot's method, which involves the rapid, often explosive, combustion of the substance with highly compressed oxygen in the so-called calorimetric bomb. Stress is laid on the regular character of the combustion in the first case, and on the irregular character of the combustion in the second. It is not matter for surprise, therefore, that the results obtained by the two methods exhibit considerable differences, and according to the author it is the faultiness of Berthelot's method which is responsible for this. In order to study the relation of heats of combustion to

constitution, the experimental data throughout must be of the same degree of accuracy, since the change in the heat of combustion corresponding with a change in the molecular structure is simply the difference of two experimental values. When this is recognised, less dependence will be placed on the data quoted by Berthelot, for these have been obtained partly by himself, partly by his pupils and other workers; there is therefore no guarantee for the equal level of accuracy of these data. All the data used by the author, on the other hand, are the result of his own personal observations and measurements.

Apart from these general considerations, a comparative study of the numerical data obtained by the two methods shows clearly the inferiority of Berthelot's method. This comparison is made (1) on hydrocarbons, which always form the starting point in the study of heats of combustion as related to constitution, and present no experimental difficulties; (2) on halogen compounds, which do present certain difficulties, and are therefore specially suitable for determining the relative value of the two methods. The author's data all refer to the gaseous condition of the substance; only the comparatively few, therefore, of Berthelot's data which refer to the same condition are comparable with the author's numbers.

I. Hydrocarbons. It may be shown that the heat of combustion of methane is increased by the same amount for each successive replacement of hydrogen by the methyl group, as will be seen from the following table:

Hydrocarbon.	Molecular formula.	Heat of combustion at constant volume.	Difference.
Methane	CH ₄	210·77 Cal.	—
Ethane	CH ₃ ·CH ₃	368·99 „	158·22
Propane	CH ₃ (CH ₃) ₂	527·47 „	158·35
Trimethylmethane	CH(CH ₃) ₃	685·16 „	158·13
Tetramethylmethane ...	C(CH ₃) ₄	844·79 „	158 50

It follows from the foregoing that the four valencies of the carbon atom are of equal value, and hence the relation between the heat of combustion of the molecule C_aH_{2b}, and its constitution may be expressed by the formula

$$f C_a H_{2b} = a.x + 2by - \Sigma v \quad \dots\dots\dots (1),$$

in which x is the heat of combustion of each carbon atom of a gaseous compound, y is the heat of combustion of each hydrogen atom linked to carbon, and Σv is the influence of all carbon linkings on the magnitude of the heat of combustion. Further, if p_1 , p_2 , and p_3 represent the numbers of single, double, and triple linkings respectively, and v_1 , v_2 , v_3 represent the heat effects corresponding with single, double, and triple linkings, then

$$\Sigma v = p_1 v_1 + p_2 v_2 + p_3 v_3 \quad \dots\dots\dots (2).$$

Evidently also:

$$2a - b = p_1 + 2p_2 + 3p_3 \quad \dots\dots\dots (3),$$

whence, combining equations (1), (2), and (3), it follows that

$$fC_aH_{2b} = a(x - 2v_1) + b(2y + v_1) + p_2(2v_1 - v_2) + p_3(3v_1 - v_3) \dots (4).$$

Since the quantities within brackets are constants, this equation may be written also :

$$fC_aH_{2b} = a.A + b.B + p_2.P_2 + p_3.P_3 \dots (5).$$

The exact values of A , B , P_2 , and P_3 can be deduced from the experimental data. Thus, from the foregoing table it is found that $A = 105.92$ Cal. and $B = 52.40$ Cal., and, from the heats of combustion of hydrocarbons with double and triple bonds, it is similarly found that $P_2 = 16.15$ Cal. and $P_3 = 44.37$ Cal. The following table gives the heats of combustion of a number of hydrocarbons calculated by the formula (5), and alongside of these the experimental values obtained by the author and by Berthelot respectively, with the corresponding differences between calculated and observed values :

Heat of Combustion of Gaseous Hydrocarbons at Constant Volume.

Hydrocarbon.	C_aH_{2b} .	Calculated. Cal.	Thomsen.		Berthelot.	
			Cal.	Diff.	Cal.	Diff.
Methane	CH_4	210.7	210.8	+0.1	212.3	+1.6
Ethane	C_2H_6	369.0	369.0	± 0.0	370.8	+1.8
Propane	C_3H_8	527.4	527.5	+0.1	526.7	-0.7
Trimethylmethane ...	C_4H_{10}	685.7	685.2	-0.5	—	—
Tetramethylmethane .	C_5H_{12}	844.0	844.8	+0.8	—	—
Ethylene.....	C_2H_4	332.8	332.2	-0.6	339.9	+7.1
Propylene ...	C_3H_6	491.1	491.3	+0.2	497.8	+6.7
isoButylene	C_4H_8	649.4	648.9	-0.5	—	—
Diallyl	C_6H_{10}	929.8	930.8	+1.0	902.3	-27.5
Acetylene	C_2H_2	308.6	309.2	+0.6	314.8	+6.2
Allylene	C_3H_4	466.9	466.4	-0.5	471.8	+4.9
Dipropargyl	C_6H_6	881.5	881.4	-0.1	852.1	-29.4

The table shows clearly the high relative accuracy of the author's data and the great irregularity of the data communicated by Berthelot. It is impossible to bring the latter's values for the heats of combustion of diallyl and dipropargyl into harmony with those for other hydrocarbons with double or triple linkings. Again, Berthelot's values for the heats of combustion of diallyl and dipropargyl are about 3 per cent. less than the author's values, whilst Berthelot's values for ethylene, propylene, acetylene, and allylene are 1—2 per cent. higher than the author's values. The great relative accuracy of the latter is further demonstrated in the following table, in which are compared the heats of combustion of carbon compounds differing from each other only by one atom of carbon :

Substance	Molecular formula.	Heat of combustion.	Difference.
Ethylene.....	C_2H_4	332.2 Cal.	} 121.4 Cal.
Methane	CH_4	210.8 „	
Propylene	C_3H_6	491.3 „	} 122.3 „
Ethane	C_2H_6	369.0 „	
isoButylene	C_4H_8	648.9 „	} 121.4 „
Propane	C_3H_8	527.5 „	
Chloroethylene	C_2H_3Cl	297.6 „	} 121.4 „
Methyl chloride	CH_3Cl	176.2 „	
Allyl chloride	C_3H_5Cl	453.7 „	} 120.6 „
Ethyl chloride	C_2H_5Cl	333.1 „	
Allyl bromide	C_3H_5Br	461.1 „	} 120.3 „
Ethyl bromide	C_2H_5Br	340.8 „	
Allyl methyl ether	$C_3H_5 \cdot O \cdot CH_3$	625.7 „	} 121.3 „
Ethyl methyl ether.....	$C_2H_5 \cdot O \cdot CH_3$	504.4 „	

The corresponding differences deduced from Berthelot's values for (1) ethylene and methane, (2) propylene and ethane, are 127.6 and 127.0 Cal.

It appears, therefore, that Berthelot's values for the heats of combustion of the olefines are about 6 Cal. too high; his values also for acetylene and allylene are found to be too high. The very unequal accuracy of Berthelot's data is especially evident in the case of these unsaturated hydrocarbons, for they tend to burn with a smoky flame, and it is only when care is taken, as in the author's method of working, to make their combustion regular and complete that satisfactory results can be obtained; for the regularity and completeness of the combustion by Berthelot's explosive method, there is no guarantee.

Again, in the author's data, there is a regular difference between the heat of combustion of an ethyl compound and that of the corresponding phenyl compound, as shown in the following table:

Compound.	Heat of combustion.	Difference.
$C_6H_5 \cdot H$	797.9 Cal.	} 428.9 Cal.
$C_2H_5 \cdot H$	369.0 „	
$C_6H_5 \cdot OH$	767.6 „	} 428.3 „
$C_2H_5 \cdot OH$	339.4 „	
$C_6H_5 \cdot O \cdot CH_3$	934.8 „	} 430.4 „
$C_2H_5 \cdot O \cdot CH_3$	504.4 „	
$C_6H_5 \cdot Cl$	762.9 „	} 429.8 „
$C_2H_5 \cdot Cl$	333.1 „	

Berthelot's value for the heat of combustion of benzene is 782.6 Cal., and the difference between the values for benzene and ethane is 411.8 Cal.

II. Halogen compounds. The differences between Berthelot's and the author's numbers for the heats of formation of halogen compounds are so great that either one or other of the two series of data must be entirely valueless. In the author's method for the combustion of these substances (see details in "Thermochemische Untersuchungen," II, 339—364, and IV, 77—127), the results were checked by an estimation of carbon dioxide, halogen hydride, and free halogen in the combustion products. In the experiments of Berthelot and his pupils, on the other hand, the halogen compound has simply been burned in the calorimetric bomb, often with the addition of camphor; in this case,

there is no guarantee that the process of combustion has been a normal one. The following table gives an idea of the differences in the results obtained. The values given in the table are the heats of formation at constant volume from amorphous carbon and gaseous chlorine, bromine, or iodine. The direct experimental data given by Berthelot refer to carbon as diamond and to constant pressure: these original values have therefore been suitably corrected to make them strictly comparable with the author's:

*Heats of Formation of Halogen Compounds (in Form of Gas or Vapour)
at Constant Volume.*

Substance.	Molecular formula.	Berthelot.	Thomsen.
Methyl chloride	CH_3Cl	30.1 Cal.	21.97 Cal.
Ethyl „	$\text{C}_2\text{H}_5\text{Cl}$	41.5 „	29.55 „
Propyl „	$\text{C}_3\text{H}_7\text{Cl}$	—	36.02 „
<i>iso</i> Butyl „	$\text{C}_4\text{H}_9\text{Cl}$	—	43.05 „
Amyl „	$\text{C}_5\text{H}_{11}\text{Cl}$	50.1 „	50.18 „ (Calcd.)
Chloroethylene	$\text{C}_2\text{H}_3\text{Cl}$	—	- 2.46 „
Chloropropylene	$\text{C}_3\text{H}_5\text{Cl}$	—	+ 7.25 „
Allyl chloride	$\text{C}_3\text{H}_5\text{Cl}$	—	+ 5.94 „
Phenyl „	$\text{C}_6\text{H}_5\text{Cl}$	—	- 12.38 „
Ethylene chloride.....	$\text{C}_2\text{H}_4\text{Cl}_2$	—	+ 33.12 „
Ethylidene „	$\text{C}_2\text{H}_4\text{Cl}_2$	37.3 „	33.07 „
Chloroacetol	$\text{C}_3\text{H}_6\text{Cl}_2$	—	40.34 „
Methylene chloride	CH_2Cl_2	32.8 „	—
Chloroform	CHCl_3	48.3 „	23.53 „
Chloroethylene chloride.	$\text{C}_2\text{H}_3\text{Cl}_3$	—	32.83 „
Tetrachloromethane....	CCl_4	70.6 „	20.45 „
Tetrachloroethylene	C_2Cl_4	49.6 „ (liq.)	- 1.73 „
Hexachloroethane.....	C_2Cl_6	106.3 „	(cryst.) —
Methyl bromide	CH_3Br	18.4 „	+ 14.21 „
Ethyl „	$\text{C}_2\text{H}_5\text{Br}$	34.1 „	21.84 „
Propyl „	$\text{C}_3\text{H}_7\text{Br}$	—	29.11 „
Allyl „	$\text{C}_3\text{H}_5\text{Br}$	—	- 1.50 „
Methyl iodide	CH_3I	17.0 „	+ 2.84 „
Ethyl „	$\text{C}_2\text{H}_5\text{I}$	26.5 „	9.93 „
Methane	CH_4	19.6 „	21.17 „
Ethane	C_2H_6	25.5 „	27.40 „
Ethylene	C_2H_4	- 11.0 „	- 3.29 „

The heats of formation of methane, ethane, and ethylene are added to the table for the sake of comparison. If the monochloro-derivatives of the paraffins are first considered, the author's values in the foregoing table show that, as usual in a homologous series, there is a simple relationship between the heat of formation of the molecule and its constitution. The heat of formation of the gaseous compound, $\text{C}_a\text{H}_{2a+1}\text{Cl}$, from amorphous carbon, gaseous hydrogen and chlorine is given by the formula: $(\text{C}_a\text{H}_{2a+1}\text{Cl}) = 15.13 \text{ Cal.} + a. 7.01 \text{ Cal.}$ The difference between the values calculated by this formula and the author's values for methyl, ethyl, propyl, and *isobutyl* chlorides does not exceed in any case 0.1 per cent. of the corresponding heat of combustion. The differences between Berthelot's and the author's values for methyl and ethyl chlorides are about 8 and 12 Cal. respectively. It is noteworthy that the only value given by Berthelot (that for amyl

chloride) which agrees with the calculated value was not the result of a determination in the calorimetric bomb.

According to the author's data, there is a constant difference between the heats of formation of corresponding chlorides, bromides, and iodides. The unequal accuracy of Berthelot's data is evidenced by the fact that his values exhibit no such regularity, as may be seen from the following :

	Methyl.	Ethyl.	Propyl.	Allyl.	
Chloride-Bromide {	7.76 11.7	7.71 7.4	6.91 —	7.44 Cal. ... — ,, ...	Thomsen Berthelot
Bromide-Iodide {	11.37 1.4	11.91 7.6	— —	— — ,, ...	Thomsen Berthelot

The difference between the heats of formation of neighbouring members of homologous series should be approximately a constant, but this is the case only with the author's data :

	Chloride.	Bromide.	Iodide.	
Ethyl-Methyl {	7.6 11.4	7.6 15.7	7.1 Cal. 9.5 ,,	Thomsen Berthelot

It may further be shown, as follows, that the author's values for the heats of formation of two analogous compounds, the molecules of which differ only by one carbon atom, exhibit a regular difference :

Chloroethylene-methyl chloride.....	- 24.4 Cal.
Chloropropylene-ethyl chloride	- 22.3 ,,
Allyl chloride-ethyl chloride	- 23.6 ,,
Tetrachloroethylene-tetrachloromethane	- 22.2 ,,

A very important criterion of the accuracy of Berthelot's data is found in a comparison of the heats of formation of methane and of its chlorine derivatives :

Substance.	Molecular formula.	Heat of formation at constant volume.	
		Thomsen.	Berthelot.
Methane	CH ₄	21.2 Cal.	19.6 Cal. }
Methyl chloride	CH ₃ Cl	22.0 ,,	30.1 ,, }
Methylene chloride ..	CH ₂ Cl ₂	—	32.8 ,, }
Chloroform	CHCl ₃	23.5 ,,	48.3 ,, }
Tetrachloromethane.	CCl ₄	20.5 ,,	70.6 ,, }
			10.5 2.7 15.5 22.3

It will be seen that, according to the author's results, chlorine and hydrogen exert a practically equal influence on the heat of formation of the molecule, whereas Berthelot's results indicate that the heat effect associated with the linking of chlorine to carbon is considerably greater than that associated with the linking of hydrogen to carbon. But it will be noted how very irregular is the increase in Berthelot's figures corresponding with the successive introduction of chlorine ; the replacement of the first half of the hydrogen in methane by chlorine raises the heat of formation 13.2 Cal. ; the similar replacement of the second half of the hydrogen raises the heat of formation further by

37.8 Cal. Similar irregularities are found in Berthelot's figures for the heats of formation (1) of ethane and its chlorine derivatives, (2) of ethylene and its chlorine derivatives. Thus, according to his figures, the introduction of the first chlorine atom in ethane *raises* the heat of formation by 16.0 Cal.; the introduction of the second chlorine atom gives a value 4.2 Cal. *below* that for ethyl chloride. In these cases, as also for benzene (heat of formation = -13.7 Cal.) and chlorobenzene (heat of formation = -12.4 Cal.), the author's data all support the view that chlorine and hydrogen exert an approximately equal influence on the heat of formation of the molecule.

Summing up, the author insists again on the high relative accuracy of his own data and their suitability for the development of relationships between heat of combustion and constitution. Berthelot's data, on the other hand, are so irregular and of such low relative accuracy that they are quite useless for any such purpose, and theoretical investigations (Lemoult, *Abstr.*, 1904, ii, 310; Lagerlöf, *ibid.*, 382, 605; this vol., ii, 76) based on these data lead to entirely wrong conclusions.

J. C. P.

General Relations between the Heats of Combustion of Organic Compounds and their Constitutional Formulæ. Calculation of the Heats of Combustion. Part II. PAUL LEMOULT (*Ann. Chim. Phys.*, 1905, [viii], 4, 5—70).—The application of the author's methods of calculating the heats of combustion of organic substances (*Abstr.*, 1903, ii, 410; 1904, ii, 12, 310) to the various classes of nitrogen, halogen, and sulphur compounds is considered. The results recorded have already been published (*Abstr.*, 1904, ii, 382: amines, amides, imides, nitriles, and heterocyclic compounds with nitrogen in the ring; *Abstr.*, 1904, ii, 605: sulphur and halogen compounds; *Abstr.*, 1904, ii, 805: miscellaneous). The "calculated" and "experimental" heats of combustion for a very large number of compounds of these classes are tabulated in the original, and these tables show the general agreement existing between the two sets of numbers.

T. A. H.

Thermochemical Investigation of Strychnine and Brucine. MARCELLIN BERTHELOT and GAUDECHON (*Ann. Chim. Phys.*, 1905, [viii], 5, 145—165).—A *résumé* of work already published (compare this vol., ii, 301).

M. A. W.

Determination of Vapour Densities at High Temperatures. II. Vapour Density of Carbon Dioxide at 2000°. FRIEDRICH EMICH (*Monatsh.*, 1905, 26, 505—523. Compare *Abstr.*, 1904, ii, 14).—By means of the apparatus described in the previous paper, the author has compared the rate of flow of carbon dioxide with that of nitrogen at the ordinary temperature and at 2000°. The results show that at 2000° carbon dioxide is not, or is only slightly, dissociated (compare Le Chatelier, *ibid.*, 1889, 205; Hahn, *ibid.*, 1903, ii, 711; Jüptner, *ibid.*, 1904, ii, 382).

The crumbling of the edges and consequent enlargement of the opening of the iridium tubes is diminished by coating the tubes with a thin layer of zirconium and yttrium oxides. The temperature of

such glazed tubes, equally with that of the unglazed iridium, can be determined with sufficient accuracy by the optical pyrometer.

G. Y.

New Apparatus for the Determination of Vapour Density.

E. GRIMSEHL (*Zeit. angew. Chem.*, 1905, 18, 734—735).—The author describes a form of apparatus for the rapid determination of vapour densities. The substance is vaporised in a tube about 130 cm. long, surrounded by a vapour jacket. Towards the upper end, this tube is open to the atmosphere, below it communicates by a 3-way stopcock with a delicate manometer consisting of two wide tubes connected with one another by a narrow bore tube, the whole containing coloured water with an air bubble as index in the horizontal tube. By this means, the difference of level is magnified about 50 times. When the tube is full of vapour, it is placed in communication with the manometer, the reading of which gives the difference between the weight of the column of vapour and that of a column of air of equal height, from which the vapour density is readily obtained.

L. M. J.

Calculation of the Exact Molecular Weights of the Easily Liquefiable Gases from their Densities; Atomic Weights of Hydrogen, Nitrogen, Argon, Chlorine, Sulphur, and Carbon.

PHILIPPE A. GUYE (*Compt. rend.*, 1905, 140, 1241—1243. Compare Abstr., 1904, ii, 475).—The relationship $M/L(1+a)(1-b)=22.412$, in which M is the molecular weight, L the weight of a litre of the gas in the normal state, and a and b the constants calculated from the critical data, is not satisfied by the more easily condensable gases. The deviations are due to the fact that the values of a and b for the critical state differ from the values for the normal condition. The correct values for the normal condition of the gas have been deduced, and the following molecular weights, referred to $O_2=32.000$ as basis, have been calculated: CO_2 , 44.003; N_2O , 44.000; SO_2 , 64.065; HCl , 36.484; C_2H_2 , 26.018. From these, the atomic weights of the contained elements are deduced. The numbers given are: hydrogen, 1.0077; carbon, 12.002; nitrogen, 14.007; chlorine, 35.476; sulphur, 32.065; and argon, 39.866. Except in the case of nitrogen, these values agree well with the numbers in the international table.

H. M. D.

Atomic Weight of Nitrogen deduced from the Ratio of the Densities of Nitrogen and Oxygen. PHILIPPE A. GUYE (*Compt. rend.*, 1905, 140, 1386—1388. Compare preceding abstract).—If d_1 and d_2 are the densities of two gases measured at corresponding temperatures T_1 and T_2 , and under corresponding pressures p_1 and p_2 , and if the molecular weights of the gases are M_1 and M_2 , then, according to the theory of corresponding states, $d_1/d_2 = M_1 p_1 T_2 / M_2 p_2 T_1$, or $M_1/M_2 = (d_1 T_1 / p_1) / (d_2 T_2 / p_2)$. The ratio of the densities of the two gases, measured at corresponding temperatures and pressures, when reduced to the normal state (0° and 760 mm.) should therefore give the ratio of the molecular or atomic weights.

When the corresponding temperatures and pressures are so chosen that the interpolation involved in the reduction is a minimum (oxygen,

100° and 760 mm., nitrogen, 37° and 505 mm.), the number deduced for the atomic weight of nitrogen is 14.014.

According to Berthelot, the two gases satisfy the simple laws with greatest exactitude at a temperature equal to $2.45 \times$ critical temperature. If these (oxygen 105°, nitrogen 40°) are taken as the corresponding temperatures, and the pressure in each case is taken as 760 mm., the atomic weight deduced is 14.011.

These numbers are compared with others obtained from density measurements by using other reduction methods, and 14.009 is considered to be the most probable value of the atomic weight of nitrogen according to density determinations.

H. M. D.

Molecular Attraction. IV. Biot's Formula for Vapour Pressure and Some Relations at the Critical Temperature.

JAMES E. MILLS (*J. Physical Chem.*, 1905, 9, 402—417. See this vol., ii, 152).—The combination of Crompton's equation for the latent heat of vaporisation with the ordinary thermodynamical equations leads to the expression $dP/dT = 2R/v$ at the critical temperature, where v is the critical volume, that is, at the critical temperature the value of dP/dT is exactly double what it would be for the perfect gas occupying the same volume. As Crompton's equation had been shown previously to give good results for the heat of vaporisation at temperatures approaching the critical temperature, the critical values for dP/dT are taken from the above expression, and shown to be in good accord with the observed values where comparison is possible—the agreement in the case of isopentane, normal pentane, and ether being within experimental errors. It is shown that in the neighbourhood of the critical temperature the Biot curve must lie below the true curve, and that no alteration of the constants will cause concordance. Employing the above relation, the values for $\mu' [(L - E)/(\sqrt[3]{d} - \sqrt[3]{D})]$ at the critical temperature agree well with the mean values found previously. From the previous results, the author is further able to deduce the well-known relation $D_c/d_c = \text{constant}$, where D_c is the theoretical, and d_c the actual critical density.

L. M. J.

Osmosis through Silica Tubes. G. BELLOC (*Compt. rend.*, 1905, 140, 1253—1254. Compare Berthelot, this vol., ii, 316).—After exposure to high temperatures, the surface of fused silica has a milky appearance. Microscopic examination shows that the surface is considerably altered, and crystalline particles are recognisable in reflected light. The phenomenon of osmosis is perhaps connected with this process of devitrification.

H. M. D.

Permeability of Glass Vessels. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 1286—1292).—The author finds that tubes of "ordinary" white glass or of Jena glass are permeable to hydrogen, oxygen, and carbon monoxide under the conditions observed for fused silica vessels (this vol., ii, 316), but at lower temperatures. No loss was observed when wood charcoal or graphite was heated in either "ordinary" or Jena glass vessels, otherwise vacuous.

The permeability of the walls of glass or fused silica vessels to

gases is regarded as similar in character to the interchange of gases which takes place through caoutchouc or animal membranes.

T. A. H.

Employment of Thermal Analysis in Abnormal Cases. GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, 45, 24—30).—In 1903 (*Abstr.*, 1904, 113), the author showed how the composition of crystallised chemical compounds occurring in alloys could be established by thermal analysis. There are two chief cases, namely, (1) the compound melts to a homogeneous liquid, (2) the compound splits up at a definite temperature into another crystalline substance and a fused mass. Under the second head, certain complications may occur during the cooling of the fused alloy; it is shown in detail that the complications do not invalidate the method.

D. H. J.

Determination of Chemical Equilibrium from Explosion Processes. I. K. FINCKH (*Zeit. anorg. Chem.*, 1905, 45, 116—126).—When electrolytic gas mixed with air is exploded under different conditions, it is found that the proportion of nitric oxide (NO) present after the explosion depends on the temperature and pressure (concentration) of the admixed electrolytic gas. It is clear then that the equilibrium which exists at the moment of the explosion cannot be deduced from the final equilibrium after cooling, and that the law of mass action cannot be applied directly. An experimental attempt was made to arrive at the same conclusion in the case of the formation of hydrogen peroxide by the explosion of hydrogen with an excess of oxygen; here the amount of peroxide obtained is much smaller than that corresponding with chemical equilibrium.

D. H. J.

Determination of Chemical Equilibrium from Explosion Processes. II. WALTHER NERNST (*Zeit. anorg. Chem.*, 1905, 45, 126—131).—With reference to Finckh's work (preceding abstract), the author points out that it would be difficult to calculate in general the displacement of the chemical equilibrium in explosion processes, but suggests that it would be possible to give a mathematical treatment in the case where (as in the formation of nitric oxide by the explosion of electrolytic gas mixed with air) the velocity of the reaction is not sufficiently great to allow of the establishment of equilibrium at the moment of the explosion. When applied to Finckh's experimental data, this suggestion gives satisfactory results. Another method of ascertaining chemical equilibrium depends on the measurement of the maximum pressure of the explosion; some applications of this method were given by Mallard and Le Chatelier (*Ann. Mines*, 1883, 8, 4).

D. H. J.

Equilibria in the Systems: $\text{TlNO}_3\text{—KNO}_3$, $\text{TlNO}_3\text{—AgNO}_3$, and $\text{TlNO}_3\text{—NaNO}_3$. CORNELIS VAN EIJK (*Zeit. physikal. Chem.*, 1905, 51, 721—731).—(1) $\text{TlNO}_3\text{—KNO}_3$.—By way of supplement and correction to the previous paper on this subject (*Abstr.*, 1900, ii, 133), it is stated that thallium nitrate solidifies in regular crystals, which are stable down to 142.5° : between 142.5° and 72.8° , the

rhombohedral modification is the stable one; below 72.8° , the rhombic modification. The latter transition point can easily be overlooked, since the transition process is very sluggish. The transition of the rhombohedral mixed crystals containing from 100—81 molecular per cent. of thallium nitrate takes place at temperatures rising gradually from 72.8° to 78° .

(2) $\text{TlNO}_3\text{—AgNO}_3$.—The substance of this communication has been already reported (Abstr., 1900, ii, 403).

(3) $\text{TlNO}_3\text{—NaNO}_3$.—The freezing point of thallium nitrate is 206.1° , that of sodium nitrate is 308° ; the freezing point curve for mixtures of the two salts is of the simplest type, with a eutectic point at 162° . There is no evidence of the formation of a double salt. Further, the transition temperatures of thallium nitrate are not altered by the addition of sodium nitrate, hence no mixed crystals are formed.

J. C. P.

Equilibrium between Acetone and Hydroxylamine Hydrochloride. PHILIPPE LANDRIEU (*Compt. rend.*, 1905, **140**, 1392—1393. Compare Francesconi and Milesi, Abstr., 1902, i, 660).—When acetone and hydroxylamine hydrochloride are brought together in aqueous solution in molecular proportions, a state of equilibrium is established, which can be represented by



The value of x has been determined for a series of concentrations by measuring the heat developed on addition of excess of sodium hydroxide to the solution. If this be denoted by Q , and if Q_1 and Q_2 are the quantities of heat developed when excess of the alkali is added respectively to acetone and hydroxylamine hydrochloride and to acetoxime hydrochloride, then $x = (Q_1 - Q)/(Q_1 - Q_2)$. The following numbers were obtained:

Litres per gram-mol.	4	6	8	12	24	48
Q_1	—	—	23.13	25.19	26.06	28.52
Q_2	18.21	20.77	21.15	22.20	24.52	—
Q	19.04	21.66	22.25	23.30	25.99	—
x	0.84	0.80	0.75	0.72	0.63	—

The values of x thus found are in agreement with the requirements of the law of mass action.

H. M. D.

Approximate Composition of the Hydrates formed by Certain Electrolytes in Aqueous Solutions at Different Concentrations. X. HARRY C. JONES and H. P. BASSETT (*Amer. Chem. J.*, 1905, **33**, 534—586. Compare Abstr., 1904, ii, 386, 710, and previous abstracts).—A series of curves based on data published in earlier papers has been constructed in order to exhibit the relation between the water of crystallisation of certain electrolytes and the depression of the freezing point of their aqueous solutions. The relations thus shown afford conclusive evidence of the existence of hydrates in the solutions.

Experiments have been carried out with the object of obtaining the data required for calculating the approximate composition of the hydrates formed at various concentrations. The depression of the freezing point, the conductivity at 0°, and the sp. gr. have been determined of solutions of different concentrations of calcium chloride and bromide, strontium bromide, barium bromide, magnesium chloride and bromide, manganese chloride and nitrate, cobalt chloride and nitrate, nickel chloride and nitrate, copper chloride and nitrate, and sulphuric acid. The results are tabulated and are also plotted as curves.

From an examination of these results, it is evident that the amount of water combined with the dissolved substance increases regularly as the concentration of the solution increases. In some cases, the number of mols. of water combined with 1 mol. of the dissolved substance increases from the most concentrated to the most dilute solution, whilst in other cases it either passes through a maximum or attains a maximum value which remains practically constant as the dilution is further increased. E. G.

Liquid Hydrogen Sulphide as a Solvent. UBALDO ANTONY and G. MAGRI (*Gazzetta*, 1905, 35, i, 206—226).—The characters exhibited by liquid hydrogen sulphide differ widely from those of the gas. When quite pure, the liquid can be kept in Dewar's vacuum vessels isolated from external moisture; it undergoes slow evaporation, which is accelerated by the addition of pieces of pumice, &c. It has a neutral reaction to litmus paper, owing either to the non-dissociation of the hydrogen sulphide or to the inactivity of the litmus at the low temperature of the liquid. Electrically, liquefied hydrogen sulphide acts as an insulator, and in the neighbourhood of its boiling point it does not exhibit in its chemical behaviour that analogy with water which would be expected from its chemical composition. As a solvent, it behaves to some extent similarly to carbon disulphide, alcohol, ether, or benzene, but although its solvent powers are relatively extended, its ability to cause dissociation is far less marked than that of water and other strongly dissociating solvents. The salts of energetic bases are not soluble in it, but non-metallic compounds are dissolved by it, giving conducting solutions. Iodine, when dissolved in liquid hydrogen sulphide, bestows on it very considerable conductivity; phosphorus iodide has the same effect to a less degree, and the haloid compounds of the other non-metals, although they dissolve in very small proportions, give solutions of moderate conductivity. Solutions of certain organic substances, for example, iodoform and tetramethylammonium iodide, yield solutions having conductivities which indicate that organic compounds may become ionised in liquid hydrogen sulphide.

The nitro-derivatives of benzene, nitronaphthalene, and naphthylamine dissolve moderately well in this solvent, but the solutions are non-conducting; there is a marked difference between the solubility of picric acid and that of potassium picrate.

Most of the above-mentioned compounds dissolve in liquid hydrogen sulphide with absorption of heat, but exceptions to this rule are met with in phosphorus trichloride and tribromide.

Hydrocarbons, alcohols, ethers, &c., also dissolve in liquid hydrogen sulphide.

The marked chemical activity of hydrogen sulphide in the state of gas or in aqueous solution vanishes almost entirely when the gas is liquefied. Thus, iodine reacts but very slightly with liquid hydrogen sulphide, but gives a dark red solution; also, liquid sulphur dioxide and liquid hydrogen sulphide mix, but only react readily in presence of an ionising liquid. Salts of copper, lead, &c., are unchanged by liquid hydrogen sulphide, and the same is the case with powerful oxidising agents such as chromium trioxide, chromates, dichromates, permanganates, &c. Concentrated sulphuric acid and Nordhausen acid are both solidified in liquid hydrogen sulphide, but do not react with it. Sodium and potassium remain unchanged in the liquid, and mercury solidifies in it without exhibiting any superficial alteration. Bromine, even in the solid condition, reacts energetically with liquid hydrogen sulphide, forming sulphur bromide.

Iodine and liquid hydrogen sulphide do not react when dissolved in ordinary solvents, such as the lower aliphatic hydrocarbons, carbon disulphide, or chloroform. Nor does the presence of thiophen determine any reaction, but decane, carvene, amylene, and benzene do so, various products being obtained. More marked in their power to cause interaction between iodine and liquid hydrogen sulphide are hydroxylated compounds, and the same is the case with aldehydes and ketones; indeed, benzaldehyde alone reacts with the liquid sulphide.

Attention is called to the papers by McIntosh and Steele (*Abstr.*, 1904, ii, 533) and Archibald and McIntosh (*Abstr.*, 1904, ii, 534) on this subject.

Descriptions, with illustrations, are given of the apparatus used for the preparation, purification, and liquefaction of the hydrogen sulphide and for the conductivity measurements.

T. H. P.

Influence of Alkaloids and Alkaloidal Salts on Catalysis.

ORVILLE H. BROWN and C. HUGH NEILSON (*Amer. J. Physiol.*, 1905, 13, 427—435).—The action of strychnine, caffeine, and their salts on the hydrolysis of hydrogen peroxide by platinum black and by aqueous extracts of kidney or pancreas has been examined. The results are given in tabular form, and show that the action exhibited is almost always inhibitory, some salts being more active in this direction than others. The salts of hydrochloric, hydrobromic, and nitric acids invariably retard the catalysis whether the base is an alkaloid or a metal. In the case of other salts, the result is either less marked, or occasionally a slight stimulating effect is noticeable with certain concentrations.

W. D. H.

Theory of Colloids. KARL LANDSTEINER (*Zeit. physikal. Chem.*, 1905, 51, 741—742).—The author draws attention to earlier work by himself and Jagič, to which Billitzer (this vol., ii, 305) has made inadequate reference.

J. C. P.

Theory of Colloids. EDUARD JORDIS (*Zeit. Elektrochem.*, 1905, 11, 288—290).—Mainly a claim for priority.

T. E.

The Unit of Combining Weights. ROBERT LUTHER (*Zeit. Elektrochem.*, 1905, 11, 273).—The chemical combining weights might be brought into harmony with the C.G.S. system of physical units (by means of Faraday's law) by defining the combining weight of a univalent element as the quantity corresponding with 10^4 electromagnetic units of electricity. This quantity of electricity is very nearly 100,000 coulombs, and the combining weights so defined would therefore be about 3·5 per cent. larger than those at present in use.

T. E.

The Conception of Valency. JEAN BILLITZER (*Zeit. anorg. Chem.*, 1905, 45, 81—82).—In answer to Abegg and Hinrichsen, the author emphasises the distinction between total affinity and valence affinity (*Abstr.*, 1904, ii, 32, 475, 720 ; this vol., ii, 155).

D. H. J.

A Simple Gas Pressure Regulator. J. MAREK (*J. pr. Chem.*, 1905, [ii], 71, 431—432).—Two forms of a simple gas pressure regulator, which can be set up with ordinary laboratory apparatus, are described and illustrated.

G. Y.

Inorganic Chemistry.

Chemical Combination of Oxygen and Hydrogen under the Action of Radium Rays. BERGER DAVIS and C. W. EDWARDS (*J. Soc. Chem. Ind.*, 1905, **24**, 266—267).—When a radium salt is dissolved in water, hydrogen is continuously liberated; the authors have now been able to obtain the reverse effect, that is, the synthesis of water, by exposing a mixture of hydrogen and oxygen to the action of radium bromide. By determining the contraction in volume of the mixed gases on removing the water by means of phosphoric oxide, and the amount of ionisation as measured by an electrometer, 13,100 molecules of water are found to be formed for each free ion produced; the ratio increases with increase of temperature. P. H.

The Mechanics of Fire. HENRY E. ARMSTRONG (*J. Soc. Chem. Ind.*, 1905, **24**, 473—480).—The paper contains a comprehensive summary of the author's views on the mechanism of the process of oxidation, most of which have been already published elsewhere (compare *Trans.*, 1903, **83**, 1088).

The subject is treated under the following heads:—Combustion of Hydrogen. Hydrocarbons. Carbon monoxide and carbon. The Retardation of combustion by oxygen. Autoxidation. It is illustrated with numerous diagrams and tables, for details of which the original paper should be consulted. P. H.

Action of the Silent Discharge on Chlorine. G. W. A. FOSTER (*Ber.*, 1905, **38**, 1781—1784. Compare Russ, this vol., ii, 381).—Chlorine, after being subjected to a silent discharge, does not carry an electrical charge, nor can any change in the density of the gas be detected. The author considers that the use by Russ of benzene as a test substance for "active" chlorine is open to criticism.

W. A. D.

Action of Oxidising Agents on Hydriodic Acid. Reactions of Hypoiodous Acid. ANTON SKRABAL (*Chem. Zeit.*, 1915, **29**, 550—554).—By the action of an excess of an oxidising agent on dilute solutions of hydriodic acid, hypoiodous and iodic acids are formed. The colour of solutions of hypoiodous acid varies from greenish-yellow to brown according to the concentration. Dilute solutions of hypoiodous acid have the odour of iodoform, whilst more concentrated solutions, owing to their decomposition, have the odour of iodine. In acid solution, hypoiodous acid decomposes into iodine and iodic acid, a change which is accelerated by the removal of one of the products of the action by the addition of iodides, by diminishing the concentration of the hydrogen ions, or by the addition of certain reducing agents. Hypoiodous acid is probably the primary product of the oxidation of hydriodic acid.

A. McK.

Constitution of Fremy's Sulphazilate and of Pelouze's Nitrosulphate. EDWARD DIVERS (*Ber.*, 1905, **38**, 1874—1878).—A reply to Hantzsch's criticisms (this vol., ii, 313). The conclusions of Haga (*Trans.*, 1904, **85**, 78) and of Divers (*Proc.*, 1903, **19**, 283; *Trans.*, 1895, **67**, 1098) are upheld.

E. F. A.

Synthesis of Hydronitric Acid [Azoimide]. ARTHUR WESLEY BROWNE (*J. Amer. Chem. Soc.*, 1905, **27**, 551—555; *Ber.*, 1905, **38**, 1825—1829).—When a solution of hydrazine sulphate in dilute sulphuric acid is treated with hydrogen peroxide, azoimide is produced, the yield under certain conditions amounting to more than 28 per cent. of that required by the equation $3\text{N}_2\text{H}_4 + 5\text{H}_2\text{O}_2 = 2\text{N}_3\text{H} + 10\text{H}_2\text{O}$.

It has been found that small quantities of azoimide can be also obtained by the action of other oxidising agents on hydrazine sulphate.

E. G.

Solubility of Phosphorus in Ether and Benzene. ANASTASIOS CHRISTOMANOS (*Zeit. anorg. Chem.*, 1905, **45**, 132—141).—The solubilities of phosphorus in ethyl ether and in benzene at various temperatures are tabulated in the original. For 100 parts of solvent, it varies in the case of ethyl ether from 0.4335 part at 0° to 1.9984 parts at 35°. In benzene, it is 1.513 parts at 0°, and increases to 10.027 at 81°.

A saturated solution of phosphorus in ether has the sp. gr. 0.7257 at 13°, 0.7187 at 19°, 0.7283 at 25°, and n_D 1.3565462 at 19°, and 1.35435 at 25°. A saturated solution in benzene has n_D 1.5129453 at 11.9°, 1.5107379 at 19°, and 1.50638 at 25°, and the sp. gr. 0.8959 at 13°, 0.8912 at 19°, 0.8875 at 22°, 0.8861 at 25°. The solutions of phosphorus in ether and benzene respectively differ in

appearance and in the phenomena observed on keeping or on evaporating the solutions on pieces of paper in the air or on watch-glasses.

D. H. J.

Preparation of Diamonds. HENRI MOISSAN (*Ann. Chim. Phys.*, 1905, [viii], 5, 174—208).—A *résumé* of work already published (compare this vol., ii, 43, 160, 166, 247).

M. A. W.

Preparation and Purification of Carbon Tetrabromide. A. VON BARTAL (*Chem. Zeit.*, 1905, 29, 377—378).—The yield of carbon tetrabromide by Wallach's method (Abstr., 1893, i, 596) may be increased from 39 per cent. to 63 per cent. by adding 1 c.c. of acetone and 8 c.c. of bromine to a solution of 150 c.c. of 25 per cent. sodium hydroxide, shaking the mixture, filtering off the precipitate, and repeating the addition of acetone and bromine to the filtrate four times in succession, the weight of tetrabromide obtained being 19.3 grams. The product is recrystallised from methyl alcohol, from which it separates in small, colourless or slightly yellow plates, which, after washing with water and drying, may be kept for several months without decomposition if not exposed to direct sunlight.

P. H.

Reciprocal Replacement of Metals in Aqueous Solutions. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1905, 27, 540—551. Compare Abstr., this vol., ii, 164).—The experiments described in this paper show that the following pairs of metals are reciprocally replaceable in aqueous solution, the first metal of each pair being more readily replaceable by the second than the second is by the first. K, Na; K, Ba; Na, Ba; Zn, Cu; Cd, Cu; Fe, Hg; Fe, Ag; Hg, Ag; Hg, Pt; Hg, Au; Ag, Au. The conditions necessary for the reverse replacements, that is, the replacement of the second metal by the first of each pair, are described. For details of the experiments, the original must be consulted.

E. G.

Action of Potassammonium on Barium Bromide. ALEXANDRE JOANNIS (*Compt. rend.*, 1905, 140, 1243—1245).—When dry barium bromide is treated with pure dry ammonia, the compound $\text{BaBr}_2 \cdot 8\text{NH}_3$ is formed. Its dissociation tension is equal to 760 mm. at 35.4° . Potassium bromide dissolves readily in liquid ammonia, and on cooling the compound $\text{KBr} \cdot 4\text{NH}_3$ separates in crystals which melt at about -45° . The vapour pressure of the crystals near the melting point is less than the atmospheric pressure. When the compound $\text{BaBr}_2 \cdot 8\text{NH}_3$ is brought into contact with potassammonium, a reaction takes place which extends over 2—3 days. Hydrogen is evolved and barium amide and potassium bromide are formed, $\text{BaBr}_2 + 2\text{NH}_3\text{K} = \text{Ba}(\text{NH}_2)_2 + 2\text{KBr} + \text{H}_2$. The potassium bromide can be removed from the reaction products by repeated washing with liquid ammonia.

H. M. D.

Revision of the Atomic Weights of Sodium and Chlorine. THEODORE W. RICHARDS and ROGER CLARK WELLS (*J. Amer. Chem. Soc.*, 1905, 27, 459—529).—Accurate determinations have been made of the values of the ratios $\text{AgCl} : \text{NaCl}$, $\text{Ag} : \text{NaCl}$, and $\text{Ag} : \text{AgCl}$.

The sodium chloride employed was obtained from various sources and purified in several different ways, but the equivalent weight from all the samples was practically identical. It is evident from these experiments that pure sodium chloride can be easily prepared and that water can be expelled from the salt by fusion without loss of chlorine. Moreover, since it was found that the equivalent weight does not vary whether the salt is fused in a vacuum or in air, it is clear that the substance does not contain appreciable amounts of occluded oxygen or nitrogen.

The silver used in this investigation was precipitated by ammonium formate and ignited in a boat of pure lime. It was found that silver fused in hydrogen yielded exactly the same proportion of silver chloride as that which had been fused in a vacuum, a result which supports Stas' conclusion that silver does not dissolve more than 0.0004 per cent. of hydrogen. The purification of silver is best effected by fusion on pure lime in an atmosphere of pure hydrogen and subsequent fusion in a vacuum.

In precipitating silver chloride from aqueous solutions, it is necessary to use very dilute solutions, as otherwise the precipitate is liable to occlude traces of other substances which cannot always be removed. A study was made of the conditions under which such impurities are occluded and eliminated; it was found that in Stas' method of adding solid sodium chloride to a solution of a silver salt some salt is always occluded in the silver chloride. Attention is directed to various points which must be taken into consideration in accurate work of this kind.

The variable solubility of silver chloride has been investigated and the precautions to be observed in estimating traces of chlorine and silver by means of the nephelometer (Abstr., 1904, ii, 287) have been ascertained. Fused silver chloride appears to contain traces of dissolved air, but the amount is extremely small, since no appreciable loss in weight occurs on subsequent fusion in a vacuum.

The results of ten experiments for determining the value of the ratio $\text{NaCl}:\text{AgCl}$ with nine samples of sodium chloride prepared in different ways gave an average of 40.780:100, whence the atomic weight of sodium is 23.017 ($\text{Ag}=107.930$; $\text{Cl}=35.455$).

In twelve other experiments made with seven different preparations of sodium chloride and three of silver, it was found that $\text{NaCl}:\text{Ag}=54.185:100$, whence the atomic weight of sodium is 23.027.

In another series of ten experiments, it was found that the ratio $\text{Ag}:\text{AgCl}=100:132.867$. Two different methods of synthesis of the silver chloride were used, and the silver employed was obtained from various sources, but the results were practically identical. From these results, it is found that if the atomic weight of silver is taken as 107.920, a value which is probably more accurate than 107.930, the atomic weight of sodium is 23.006 and that of chlorine 35.470; if the atomic weight of silver is taken as 107.930, that of sodium becomes 23.008 and that of chlorine 35.473.

These new values affect considerably the figures in the second decimal place of all the atomic weights depending on those of chlorine, sodium, or silver, and render necessary a recalculation of all the atomic weights.

The paper contains a very full discussion of the sources of error in Stas' experiments. E. G.

Reactions with Sodium Thiosulphate. FRANZ FAKTOR (*Chem. Centr.*, 1905, i, 1524; from *Pharm. Post.*, 38, 219. Compare Abstr., 1902, ii, 256).—When sodium thiosulphate is boiled with magnesium ribbon, magnesium hydroxide and hydrosulphide are formed. When iron powder (*ferrum limatum*), sheet silver, copper shavings, or lead foil is heated with sodium thiosulphate, the black metallic sulphides are formed, whilst bismuth yields the brown sulphide and cadmium forms a yellow solution. Rose's metal on warming with the thiosulphate forms black flakes of lead and bismuth sulphides; on boiling with sodium hydroxide, the solution becomes yellow and a sulphide is formed. Alkaline solutions of thallium salts give a white precipitate with sodium thiosulphate which dissolves on boiling, forming a brown solution; brownish-black thallous sulphide, Tl_2S , separates out on the addition of hydrochloric, sulphuric, or acetic acid. When hot solutions of sodium thiosulphate and thallium salts are mixed, the liquid becomes brown. Thallous chloride, $TlCl$, is readily soluble in a solution of sodium thiosulphate, thallous bromide less so, and the iodide is insoluble.

Thallous dichromate, $Tl_2Cr_2O_7$, is an orange-yellow precipitate, which is somewhat soluble in water and dissolves in a solution of sodium thiosulphate forming the yellow chromate, Tl_2CrO_4 . When the solution of dichromate in sodium thiosulphate is warmed with ammonium chloride, chromium hydroxide, $Cr_2(OH)_6$, is precipitated. Mercurous chloride dissolves in sodium thiosulphate, and the solution forms a black precipitate on heating; when the solution is boiled with gold chloride, mercury and gold sulphide, Au_2S_3 , separate and mercuric chloride may be estimated in the filtrate. When mercuric oxide is heated with sodium thiosulphate, the red sulphide is formed, and the red sulphide under similar conditions becomes of a more brilliant tint.

E. W. W.

Electrolytic Deposition of Silver. RALPH C. SNOWDON (*J. Physical Chem.*, 1905, 9, 392—398).—The experiments were performed chiefly with a view to ascertaining the possibility of obtaining a plating deposit of silver from the solution of the nitrate. It was found that a good, coherent, finely-crystalline deposit can be obtained by rapid rotation of the cathode and separation of the anodic and cathodic liquids, and the author considers that if means for a higher speed of rotation were available, burnished deposits would result. The addition of small quantities of glue to the solution had remarkable effects, smooth, bright purple or yellow deposits with no visible crystalline structure being obtained, which resemble some of Carey Lea's deposits from organic salts. L. M. J.

Colloidal Silver. ALEXANDER GUTBIER and GUSTAV HOFMEIER (*Zeit. anorg. Chem.*, 1905, 45, 77—80).—The authors describe colour phenomena seen on forming colloidal silver in presence of gum arabic, which bear on Blake's suggestion (Abstr., 1904, ii, 31) of the existence of three (or four) allotropic coloured forms of silver. Fifty c.c. of gum arabic solution (1 : 100) were mixed with (1) 100 c.c.

of silver nitrate solution (1 : 1000) and 50 c.c. of water ; (2) 25 c.c. of silver nitrate and 125 c.c. of water ; (3) 10 c.c. of silver nitrate and 140 c.c. of water ; (4) 5 c.c. of silver nitrate and 145 c.c. of water ; (5) $1\frac{1}{2}$ c.c. of silver nitrate and 148.5 c.c. of water ; the solutions (each 200 c.c.) thus prepared were reduced by hydrazine hydrate (1 : 2000) and the hydrosols of silver obtained were purified by dialysis. The colours of the hydrosols varied with the concentration, and were for the five cases dark olive-green, olive-green, brownish, grey, and greyish respectively by reflected light ; brownish-red, red, dark violet, violet, faint violet respectively by transmitted light.

Hydrosols obtained by reduction of ammoniacal silver nitrate with phenylhydrazine hydrate are black by reflected light, green by transmitted light.

With hypophosphorous acid as reducing agent in presence of gum arabic, a light brown solution is obtained, which becomes dark brown and then deep red. If this liquid is now heated slowly to boiling, it becomes deep brown, then olive-green ; the olive-green colour continues even after dialysis.

D. H. J.

Action of Carbon Monoxide on Silver Oxide. Detection of Traces of the Gas in the Atmosphere. HENRI DEJUST (*Compt. rend.* 1905, 140, 1250—1252. Compare Gautier, *Abstr.*, 1898, ii, 535).—When carbon monoxide acts on dry silver oxide at the ordinary temperature, a considerable amount of heat is developed and metallic silver is formed : $\text{Ag}_2\text{O} + \text{CO} = \text{Ag}_2 + \text{CO}_2 + 61.2 \text{ Cal.}$ It is sometimes necessary to raise the temperature of the oxide to 40—50° before the reaction sets in. The gas also acts slowly on the oxide suspended in water ; metallic silver is deposited and a yellowish-brown solution is formed which also deposits silver. The reaction takes place much more rapidly in ammoniacal solution ; the colourless solution turns brown, then black, and deposits silver. A simple means of utilising this reaction for the approximate estimation of carbonic oxide in the air is described.

H. M. D.

Metallic Calcium. II. KURT ARNDT (*Ber.*, 1905, 38, 1972—1974. Compare *Abstr.*, 1903, ii, 76 ; this vol., ii, 87).—The author describes three alloys of aluminium and calcium, containing 23.4, 41.79—45.44, and 80.55—83.32 per cent. of calcium respectively. They had the sp. gr. 2.18, 2.26—2.38, and 1.74—1.81 respectively, and melted at 765° (corr.), 1050°, and 600° respectively. When the percentage of aluminium in the alloy is high, calcium may be separated from aluminium by distillation under diminished pressure.

Alloys of calcium and aluminium may be prepared by electrolysis fused calcium chloride with fused aluminium as the cathode.

A. McK.

Calcium Sulphate in Ammonium Sulphate Solution. EUGENE C. SULLIVAN (*J. Amer. Chem. Soc.*, 1905, 27, 529—539).—Determinations of the solubility of calcium sulphate in water and in solutions of ammonium sulphate at 25° have given the following results. The solubility in water is 0.2083 gram per 100 c.c. On the first addition of ammonium sulphate to the aqueous solution, a notable decrease in

the solubility of the calcium sulphate is observed. As the concentration of the ammonium sulphate increases, the fall becomes more gradual, and the solubility passes through a minimum equal to about two-thirds of its original value when the concentration is about 0.09 mol. per litre. From this point, the solubility gradually increases until the concentration of the ammonium sulphate is 0.6 mol. per litre, when the solubility of the calcium sulphate has the same value as in pure water. With 3 mols. of ammonium sulphate per litre, the solubility of calcium sulphate is twice as great as in water. The curve expressing the results is similar to that obtained by Seidell and Cameron (Abstr., 1902, ii, 207) for solutions of calcium sulphate and sodium sulphate.

The specific conductivity of concentrated ammonium sulphate solutions is decreased by saturation with calcium sulphate. On the assumption that ammonium sulphate is dissociated into 2NH_4^+ and SO_4^{--} , and calcium sulphate into Ca^{++} and SO_4^{--} , and that the conductivity is a measure of such dissociation, the solubility of calcium sulphate in dilute ammonium sulphate is greater than that required by the mass law.

The results are in accordance with the isohydric principle of Arrhenius (Abstr., 1899, ii, 201). The calculations show that the concentration of the non-dissociated calcium sulphate decreases as the amount of ammonium sulphate is increased. E. G.

Calcium Carbonate. II. Precipitation. WILHELM MEIGEN (*Chem. Centr.*, 1905, i, 1363—1364; from *Ber. naturfor. Ges. Freiburg i. Br.*, 15, 38—54, 55—74. Compare *ibid.*, 13, 40).—From the results of 36 experiments in which calcium carbonate was precipitated from the nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in various ways by means of normal sodium carbonate, sodium hydrogen carbonate, ammonium carbonate, and potassium carbonate, the following conclusions have been drawn. Calcium carbonate always separates from a mixture of cold solutions of the nitrate and alkali carbonate in an amorphous state and may remain in this condition for several days. When the solutions are hot, the precipitate probably also separates in an amorphous form, but cannot be isolated in this condition owing to the rapidity with which it changes into the crystalline form. The amorphous carbonate may become crystalline in either the calcite or aragonite form. The aragonite form always separates from cold solutions as spherical or globular aggregations, and from hot solutions in needles; the latter is a much less stable form. Normal sodium carbonate precipitates calcium carbonate from cold concentrated solutions, principally in the form of globular aragonite. Dilute solutions do not so readily yield aragonite, and the change of this form to calcite takes place more rapidly in such solutions. In hot solutions, calcite is readily precipitated; when aragonite is formed, it separates in needles and is more stable when precipitated from dilute solutions. In cold solutions, sodium hydrogen carbonate yields principally calcite, and when the solutions are dilute no trace of aragonite is formed; from hot solutions, however, aragonite separates in the form of very stable needles. The precipitate obtained by adding ammonium carbonate to cold concentrated solutions

consists of aragonite globules, but in dilute solutions aragonite is not formed; both kinds separate together from hot solutions. The addition of ammonia aids the formation of aragonite. Sodium carbonate and potassium carbonate throw down amorphous calcium carbonate from cold concentrated solutions. On the whole, calcium nitrate behaves like calcium chloride, but in the former case, when aragonite is formed, it is more stable than in the latter, since the presence of excess of nitrate has less effect on the precipitation. The calcite form is precipitated from solutions of calcium sulphate by all carbonates except normal sodium carbonate, which gives aragonite. From zinc solutions, aragonite effects more complete precipitation than calcite, but in the case of copper the inverse is true. Copper is completely precipitated by calcite from a solution of the nitrate in 8 hours, but aragonite requires a much longer time. Lead is also precipitated by both forms, but more quickly by aragonite. The precipitation of silver from concentrated solutions is similar to that of lead or copper.

III. *Behaviour of Calcium Carbonate towards Cobalt Salts* (compare *Centr. Min.*, 1901, 577).—By the action of finely divided aragonite on concentrated solutions of cobalt nitrate, a lilac-coloured precipitate, $2\text{CoCO}_3, 3\text{Co}(\text{OH})_2, \text{H}_2\text{O}$, is formed; it may be heated at $80\text{--}85^\circ$ without decomposing, but loses $1\text{H}_2\text{O}$ at 95° . The blue precipitate formed by calcite under similar conditions has probably the composition $\text{CoCO}_3, 3\text{Co}(\text{OH})_2$. The lilac-coloured precipitate, prepared by adding aragonite to more dilute solutions of the nitrate, has the composition, $\text{CoCO}_3, 2\text{Co}(\text{OH})_2$; finely divided calcite gives a precipitate of the same composition and colour under similar conditions, but in other cases the precipitate is probably a mixture of the blue basic carbonate with more or less hydroxide. The precipitates formed by aragonite resist the action of oxidising agents much more than those formed by calcite. Solutions of cobalt chloride behave, on the whole, in a similar way, but the precipitates always contain chlorine, and the longer the duration of the action the greater the quantity of chlorine in the precipitate; a basic cobalt chloride, $\text{CoCl}_2, \text{Co}(\text{OH})_2, 5\text{H}_2\text{O}$, is probably formed. By the action of calcite and aragonite on solutions of cobalt sulphate, blue- and lilac-coloured precipitates are formed respectively, but the latter on boiling also becomes blue; both precipitates contain considerable quantities of sulphuric acid.

E. W. W.

Strontium-ammonium. ROEDERER (*Compt. rend.*, 1905, 140, 1252—1253).—By the action of pure dry ammonia on strontium at -60° , reddish-brown crystals of strontium-ammonium are formed which dissolve in excess of ammonia to a deep blue solution.

The dissociation tension of the crystals is about 10 mm. at -40° and 760 mm. at $+46^\circ$. Analysis of the crystals which remain when the ammonia solution is evaporated at different temperatures gave $\text{Sr}, 6.38\text{NH}_3$ at -60° , $\text{Sr}, 6.15\text{NH}_3$ at -23° , and $\text{Sr}, 6.01\text{NH}_3$ at 0° . The probable formula is $\text{Sr}, 6\text{NH}_3$, analogous to that of the barium compound.

H. M. D.

Some Reactions with Magnesium. FRANZ FAKTOR (*Chem. Centr.*, 1905, i, 1305; from *Pharm. Post.*, 38, 153).—By the action of

magnesium ribbon on sodium thiosulphate, magnesium hydroxide and hydrogen are formed, whilst magnesium powder under similar conditions becomes greyish-black, and on the addition of hydrochloric acid gives off hydrogen sulphide. With a solution of iodine, magnesium iodide is formed and the liquid becomes green. Potassium dichromate and potassium permanganate are reduced by magnesium, the former to chromate. By the action of the metal on salts of antimony (antimony trichloride or potassium antimony tartrate), hydrogen and antimony hydride are liberated, whilst antimony separates in the form of black flakes. Bismuth is deposited as a black powder from solutions of the chloride or nitrate, and solutions of gold and platinum salts are reduced to the metal with liberation of hydrogen. Salts of silver are also reduced, but hydrogen is not formed. By the action of magnesium on zinc, cadmium, stannous, or bismuth salts, the metallic hydroxide and hydrogen are formed. Grey metallic thallium separates from thallium salts, and hydrogen is liberated, whilst thallium alum first yields the metal and then the hydroxide. Yellow uranyl oxide and blue molybdenum oxide are formed by the action of magnesium on uranyl salts and ammonium molybdate respectively.

In order to test for aldehydes, a solution of magenta is heated with a few pieces of magnesium ribbon until the colour disappears. An intense violet-red coloration is formed on the addition of an aldehyde. When magnesium powder is used, the solution should be filtered before adding the aldehyde. A solution of quinone becomes brown when warmed with magnesium; potassium ferricyanide is converted into ferrocyanide, and a solution of indigo is rapidly decolorised.

E. W. W.

Equilibrium between Magnesium and Sodium Sulphates.

R. BECKETT DENISON (*Trans. Faraday Soc.*, 1905, i, 136—139).—At 25°, only one double salt of these components has been obtained, namely, blödite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, whilst at somewhat higher temperatures two others appear: loewite, $\text{Na}_4\text{Mg}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$, and vanthoffite, $\text{Na}_6\text{Mg}(\text{SO}_4)_4$. The author's experiments were made with a view to ascertaining whether a double salt analogous to langbeinite, $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, was not capable of existence. Dilatometric experiments as well as tensimetric measurements with a Bremer-Frowein tensimeter indicated that a sodium-langbeinite cannot exist in contact with solution, at least up to 90°, and that at about 59° blödite in presence of MgSO_4 changes into loewite.

L. M. J.

New Oxyhaloids of Mercury. THEOPHILE FISCHER and H. VON WARTENBERG (*Chem. Zeit.*, 1905, 29, 308).—Mercurous oxychloride, HgCl, HgO , forms small, red prisms, mercurous oxybromide, HgBr, HgO , dark red, slender, rhombic plates (crystal angles 89° and 91°), and mercurous oxyiodide, $\text{HgI}, 3\text{HgO}$, brownish-red, rhombic plates. The compounds were obtained by heating the corresponding mercurous haloids with mercuric oxide and water in sealed tubes for 48—80 hours at 160—180°.

P. H.

Action of Sodium Nitrate on Native Sulphides. JOH. MATUSCHEK (*Chem. Zeit.*, 1905, **29**, 510—511).—The author states that under certain conditions galena yields a considerable quantity of metallic lead when heated in a crucible with sodium nitrate. A portion of the metal may be similarly obtained from black antimony, copper glance, and silver glance.

Lead introduced into melted nitre to which some potassium chlorate has been added yields red lead in a somewhat granular form.

L. DE K.

Existence of a Definite Lead Potassium Sulphate. FRANK G. BELTON (*Chem. News*, 1905, **91**, 191).—When a 10 per cent. solution of lead nitrate is digested at 75° with a saturated solution of potassium sulphate, white, amorphous lead potassium sulphate, $\text{PbK}_2(\text{SO}_4)_2$, is obtained. It is decomposed readily by water.

When potassium salts are present in excess, lead salts should be precipitated in the presence of excess of sulphuric acid and at the boiling point.

D. A. L.

Salts of Cerium. HERMANN WOLFF (*Zeit. anorg. Chem.*, 1905, **45**, 89—115).—In the following, P denotes the percentage of anhydrous salt dissolved in the saturated aqueous solution.

Ceric ammonium nitrate, $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$. The values of P found were : at 25°, 58.49 ; at 35.2°, 61.79 ; at 45.3°, 64.51 ; at 64.5°, 66.84 ; 85.6°, 69.4 ; at 122°, 88.03. For the interval from 25° to 85°, the interpolation formula, $P = 52.07 + 0.314t - 0.0013t^2$, expresses the results. Above 60°, there is a partial reduction of the ceric salt in solution to cerous salt ; towards the boiling point of the saturated solution, say 122°, the proportion of cerous salt present is considerable (9.8 per cent. in one case after 3 hours' boiling).

Cerous ammonium nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$. This salt is stable in aqueous solutions at temperatures from 9—55°. The experimental values of P were : at 8.75°, 70.2 ; at 25.0°, 74.8 ; at 45°, 80.4 ; at 60°, 87.2 ; at 65.06°, 89.1. The solubilities from 25—65° are expressed by the formula $P = 68.7 + 0.172t + 0.002t^2$. Solubilities at higher temperatures cannot be determined, as the salt melts in its water of crystallisation at 74°.

Cerous ammonium sulphate, $\text{Ce}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ and $\text{Ce}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$.

The experimental values of P were : at 22.3°, 5.061 ; at 22.35°, 5.058 ; at 35.1°, 4.928 ; at 45.2°, 4.755 ; at 45.0°, 2.907 ; at 55.2°, 2.140 ; at 55.3°, 2.191 ; at 75.4°, 1.46 ; at 85.2°, 1.17. A graphic representation of the results shows a curve with two branches corresponding with the hydrated and anhydrous salts ; at 45°, it is possible to obtain two saturation concentrations, corresponding with the hydrated and non-hydrated salts. In the solid state, the hydrated salt loses $6\text{H}_2\text{O}$ at 100°, the remaining $2\text{H}_2\text{O}$ not until 150°. By the action of cerium carbonate on propionic, butyric, and isobutyric acids, cerium salts similar to the known formate and acetate have been prepared.

Cerous formate, $\text{Ce}(\text{CHO}_2)_3$. Values of P found were : at 13°,

0.398; at $75^{\circ}3'$, 0.374; the solubility is therefore intermediate between the solubilities of lanthanum and didymium formates.

Cerous acetate, $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3, 1\frac{1}{2}\text{H}_2\text{O}$, is also less soluble in hot water than in cold. Solubilities found: *P* at 15° , 19.61; at $76^{\circ}2'$, 12.97.

Cerous propionate, $\text{Ce}(\text{C}_3\text{H}_5\text{O}_2)_3, \text{H}_2\text{O}$ (from warm solutions), $\text{Ce}(\text{C}_3\text{H}_5\text{O}_2)_3, 3\text{H}_2\text{O}$ (from cold solutions). *P* at 15° , 18.99; at $76^{\circ}4'$, 15.93.

Cerous butyrate, $\text{Ce}(\text{C}_4\text{H}_7\text{O}_2)_3$, crystallises in the anhydrous condition from hot alcohol (in which it is sparingly soluble) and with $3\text{H}_2\text{O}$ from cold aqueous solutions. *P* at 11° , 3.544; at 15° , 3.406; at $76^{\circ}9'$, 1.984.

Cerous isobutyrate, $\text{Ce}(\text{C}_4\text{H}_7\text{O}_2)_3, 3\text{H}_2\text{O}$. Values of *P*: at $20^{\circ}4'$, 6.603; at $75^{\circ}8'$, 3.39.

Cerous chloroacetate, $\text{Ce}(\text{C}_2\text{H}_2\text{ClO}_2)_3, 1\frac{1}{2}\text{H}_2\text{O}$, is obtained by dissolving cerium carbonate in chloroacetic acid and evaporating; it forms long needles.

Cerous trichloroacetate, $\text{Ce}(\text{C}_2\text{Cl}_3\text{O}_2)_3, 3\text{H}_2\text{O}$, is obtained by dissolving cerium in the acid and evaporating in a vacuum; it forms long needles. If an aqueous solution of the salt is boiled, the whole of the cerium separates as carbonate. The trichloroacetate is not oxidised by hydrogen dioxide, and thus differs from the cerium salts of the other organic acids mentioned previously.

D. H. J.

New Spectrum of Gadolinium. GEORGES URBAIN (*Compt. rend.*, 1905, 140, 1233—1234).—New lines in the ultraviolet absorption spectrum of gadolinium are recorded. The same results were obtained for gadolinium extracted from monazite, xenotime, and pitchblende. The metal showed the phosphorescence spectrum which has been attributed by Crookes to victorium. The author does not consider that this element and gadolinium have been definitely shown to be distinct from one another.

H. M. D.

Purification of Praseodymium. CHARLES BASKERVILLE (*Zeit. anorg. Chem.*, 1905, 45, 86).—In reply to Meyer (*Abstr.*, 1904, ii, 734), the author insists on the efficiency of Baskerville and Turrentine's method of obtaining pure praseodymium compounds (*Abstr.*, 1904, ii, 261).

D. H. J.

Properties of some Anhydrous Chlorides of Rare Metals. CAMILLE MATIGNON (*Compt. rend.*, 1905, 140, 1339—1341. Compare *Abstr.*, 1904, ii, 340, 341; this vol., ii, 391, and Muthmann and Stützel, *Abstr.*, 1900, ii, 142).—The liquids produced by melting the chlorides of lanthanum, praseodymium, neodymium, or samarium solidify to masses of deliquescent needles closely resembling in form the crystals of bacillary aragonite. Lanthanum chloride is colourless at all temperatures, has a sp. gr. 3.947 at $18^{\circ}/4^{\circ}$, and melts at 907° . On solution in water, it develops 31.3 Cal. at 17° , and the heat of formation from the oxide and hydrogen chloride is 80.3 Cal. Praseodymium chloride has a sp. gr. 4.017 at $18^{\circ}/4^{\circ}$ and melts at 818° . The heat of formation from the oxide and hydrogen chloride is 73.9 Cal. (compare *Abstr.*, 1902, ii, 263). Neodymium chloride is pink with a violet

tinge, and becomes green at its melting point; it has a sp. gr. 4.195 at $18^{\circ}/4^{\circ}$, melts at 785° , and on solution in water develops 35.4 Cal. at 17° . The heat of formation from the oxide and hydrogen chloride is 71.6 Cal. (compare Abstr., 1901, ii, 602). Samarium chloride is straw-yellow, and the tint deepens with increase of temperature. It has a sp. gr. 4.465 at $18^{\circ}/4^{\circ}$, melts at 686° , and on solution in water develops 37.4 Cal. at 17° . The heat of formation is 64.2 Cal. (compare Abstr., 1902, ii, 505).
T. A. H.

Transformation of Oxides and Oxygenated Metallic Salts into Anhydrous Chlorides. Application to Analysis. CAMILLE MATIGNON and F. BOURION (*Ann. Chim. Phys.*, 1905, [viii], 4, 127—136).—A *résumé* of work already published (Abstr., 1904, ii, 340, 341). Aluminium chloride was prepared by the general method (*loc. cit.*) from alumina, and samarium chloride from samarium sulphate.
T. A. H.

Colloidal Ferric Chlorides. G. MALFITANO (*Compt. rend.*, 1905, 140, 1245—1247).—Solutions containing 5 grams of ferric chloride per litre were maintained at 40° and the hydrolysis followed by measurement of the electrical conductivity. This having become nearly constant, the solutions were filtered through a collodion membrane and the precipitated colloid analysed. Similar experiments were made with solutions heated at 100 — 130° . The percentage of chlorine in the precipitated residues is very variable. The formulæ $\text{Fe}_2\text{Cl}_6 \cdot n\text{Fe}_2(\text{OH})_6$ ($n = 1.5$ — 7.2) and $\text{HCl} \cdot n\text{Fe}_2(\text{OH})_6$ ($n = 1.1$ — 6.7) are employed to express the composition of the precipitates from the cold and the hot solutions.
H. M. D.

Solubility of Ferric Oxide in Hydrofluoric Acid. ERNST DEUSSEN (*Zeit. angew. Chem.*, 1905, 18, 813—815).—The author has determined the solubility of ferric oxide in hydrofluoric acid, hydrochloric acid, and oxalic acid respectively at 25° . Hydrofluoric acid dissolves rust more quickly than does hydrochloric acid, and may with advantage be used for the removal of rust from laboratory apparatus.
A. McK.

Electrolytic Precipitation of Nickel on Nickel. RALPH C. SNOWDON (*J. Physical Chem.*, 1905, 9, 399—401).—When nickel work has to be replated, it must be entirely freed from the previous deposit of nickel, as otherwise the deposit does not adhere, but readily peels off. The author's experiments show that if the nickel be made the cathode in an acid solution and a fairly large current be passed for a short time, it will, if quickly washed and transferred to the plating solution, take a smooth, adherent deposit capable of burnishing. The author considers this behaviour to be due to the presence in the nickel of a thin film of oxide which cannot be removed except by vigorous reduction.
L. M. J.

Nickelic Salts. CARL TUBANDT (*Zeit. anorg. Chem.*, 1905, 45, 73—76).—Up to the present, the sesquioxide is the only tervalent compound of nickel known.

By the electrolysis of a strong solution of either (1) potassium hydrogen carbonate, in presence of a nickel anode and with employment of a current of 1 to 2 amperes per sq. dcm., or (2) of nickel carbonate in strong potassium hydrogen carbonate solution in presence of platinum electrodes and with employment of a current of 0.1 to 1 ampere per sq. dcm., an unstable red solution of a nickelic salt is obtained, which becomes quite colourless an hour after the interruption of the current, and (from the stronger solutions) deposits black nickel oxide. The solution may be filtered through glass wool, but is partly decomposed by paper filters; the colour is discharged by hydrogen peroxide, any percarbonate or persulphate, chlorine or bromine. The red liquid liberates iodine from potassium iodide, and thus a quantitative estimation of the oxygen combined with one atom of nickel may be made, with the result that the nickel is found to be in the tervalent form. The new nickelic salt has not been isolated.

D. H. J.

Electrolytic Chromium. HECTOR R. CARVETH and B. E. CURRY (*J. Physical Chem.*, 1905, 9, 353—380. See this vol., ii, 394).—The authors first review previous work on the electrolysis of chromic acid, and find that amongst other points this still leaves doubtful the question whether or not metallic chromium may be deposited in the electrolysis of chromic acid solution, and if so what are the conditions. Their own results showed that with an impure acid, chromium was deposited, this occurring instantaneously at 18° for a current density of about 80 amperes per sq. decimetre. With pure acid, the deposition was also obtained, but not so readily as with the impure acid; the decomposition voltage was found to be 2.31 volts. The effect of sulphuric acid was marked in increasing the deposition of metal, and in some cases more than one-half the total chromium was removed as metal. In all cases, the solution was coloured brown, and chromic salts were produced; a brown precipitate was also formed at the cathode, this being probably CrCrO_4 . The authors consider it probable that sexavalent chromium cations are present in the solutions of chromic acid, and that the increase of deposition caused by sulphuric acid is due to the increase of concentration of these cations, owing to a reaction of CrO_3 with the acid. It was found that the electrolytically deposited chromium can occlude about 250 times its volume of hydrogen, 24.6 c.c. being obtained from 0.698 gram of metal.

L. M. J.

A Variable Velocity Reaction of Green Chromic Sulphate. ALBERT COLSON (*Compt. rend.*, 1905, 140, 1451—1454. Compare this vol., ii, 94).—Further evidence in favour of the constitutional formula

$\text{SO}_4 \begin{smallmatrix} \text{Cr} \cdot \text{SO}_4 \\ | \\ \text{Cr} \cdot \text{SO}_4 \end{smallmatrix}$, suggested for the green chromic sulphate, is afforded by

the behaviour of the salt towards barium chloride; in boiling solutions, the decomposition of the mixture $\text{Cr}_2(\text{SO}_4)_3 + 3\text{BaCl}_2$ is complete in a few minutes, but at the ordinary temperature there is a discontinuity in the reaction; the addition of 1 mol. BaCl_2 to 1 mol. $\text{Cr}_2(\text{SO}_4)_3$ causes an immediate precipitation of BaSO_4 with a heat development of 7.15 Cal., whilst the addition of 2 to 3 mols. BaCl_2 to 1 mol. $\text{Cr}_2(\text{SO}_4)_3$ is

followed by an immediate precipitate, but the liquid remains turbid for an indefinite period, and the heat developed does not exceed 7.6 Cal.

M. A. W.

Higher Oxidation Products of Chromium. E. H. RIESENFELD, H. E. WOHLERS, and W. A. KUTSCH (*Ber.*, 1905, **38**, 1885—1898).—By the direct oxidation of chromate solutions with hydrogen peroxide in alkaline solution below 0°, salts of the hypothetical acid H_3CrO_8 have been obtained. The *ammonium* salt, $(\text{NH}_4)_3\text{CrO}_8$, crystallises in small, reddish-brown, doubly refractive octahedra, with a red reflex; the *sodium* salt forms reddish-yellow, doubly refractive, glistening plates, and decomposes with evolution of oxygen to an amorphous, bright yellow powder; the *potassium* salt is somewhat darker in colour than the ammonium, but in other respects resembles it. In acid solution, blue salts such as KH_2CrO_7 and $(\text{NH}_4)\text{H}_2\text{CrO}_7$ are formed on oxidation with hydrogen peroxide. The red salts decompose in neutral or alkaline solution into chromate, whilst in acid solution perchromic acid is formed, and is instantly reduced to a chromic salt. For the analysis of these salts, a special method based on the gasometric estimation of the oxygen evolved is described in detail. The red salts described by Hofmann and Hiendlmaier (*Abstr.*, 1904, ii, 410) have also been prepared and carefully analysed, and proved to have the formula $(\text{NH}_4)_3\text{CrO}_8$, and not $(\text{NH}_4)_2\text{CrO}_6$, as assumed by these authors. E. F. A.

Metastannic and Metazirconic Acids. JAKOB M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1905, **45**, 83—85).—Ruer (this vol., ii, 256) gave to metazirconic acid dried at 100° the formula $3\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$; the author suggests that the proportion of water found by Ruer in his experiments was accidental, and emphasises in this connection the analogy between metastannic and metazirconic acids. D. H. J.

Separation of Thorium and the Cerite Earths by Normal Sodium Sulphite. ALEXANDER BATĚK (*Zeit. anorg. Chem.*, 1905, **45**, 87—88).—The method of separation used by Grossmann (this vol., ii, 326) had been already described by the author (*Bohemian Acad. Sci. Prag*, 1902). For the separation, the basic sulphates are suspended in water (Bunsen-Brauner method) and treated for 2 hours with a rapid stream of sulphur dioxide; from the filtrate, basic sulphate is again prepared and treated with sulphur dioxide; after four operations, a sulphate is obtained practically free from didymium. By continued fractional treatment with sulphur dioxide, the basic neodymium and praseodymium sulphates may be separated from the less basic cerium sulphate, as the former are more easily converted by sulphur dioxide into soluble normal sulphates. D. H. J.

Alloys of Copper and Bismuth. ARTHUR H. HIORNS (*Trans. Faraday Soc.*, 1905, **1**, 179—186).—An account of the appearance and micro-structure of alloys of copper and bismuth is given, and the freezing point curve is described. The latter consists of four branches; from the freezing point of bismuth, the curve falls to a freezing point 245° at 97 per cent. bismuth; it then rises rapidly, reaching 600° at 95 per

cent., after which it rises more slowly, so that with from 70 to 57 per cent. of bismuth it is almost horizontal. At 57 per cent. a break occurs and the curve rises to a maximum at 1039° for 95 per cent. copper, whence it falls to the eutectic point for pure copper in contact with a solution of bismuth in copper. A number of reproductions of photographs of polished and etched surfaces of the alloys are given in the paper.

L. M. J.

Red Colloidal Solution of Gold obtained by means of Carbon Monoxide. JULIUS DONAU (*Monatsh.*, 1905, 26, 525—530. Compare Zsigmondy, *Abstr.*, 1898, ii, 522; 1900, ii, 397; 1902, ii, 188).—Bright red to purple liquid hydrosols of gold are obtained by passing a current of carbon monoxide or carbon monoxide, diluted with carbon dioxide, through solutions of auric chloride in conductivity water containing 0.002—0.05 per cent. of gold. If ordinary distilled water or tap-water is used, or if the solution is dialysed through a porous cell, the presence of a protecting agent such as gelatin or gum arabic is necessary to the stability of the hydrosol. A liquid hydrosol containing 0.005 per cent. of gold can be concentrated to 1/30 of its volume by boiling in a vacuum before precipitation takes place. The liquid hydrosol is decolorised when shaken with animal charcoal, barium sulphate, powdered porcelain, amorphous silica, fibres of filter paper, and electrolytes. These precipitations are diminished or prevented by the presence of gum arabic or gelatin. The conversion of auric chloride into colloidal gold by carbon monoxide is complete, as a liquid hydrosol, after precipitation with hydrochloric acid and filtration, yields a filtrate containing no gold. On electrolysis of the colloidal gold solution, phenomena are observed resembling those described by Blake (*Abstr.*, 1904, ii, 130).

The formation of the red liquid hydrosol of gold is observed on shaking a dilute solution of auric chloride with a litre of air containing 1 c.c. of carbon monoxide.

G. Y.

Gold-lead Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1905, 45, 11—23).—With the aid of cooling curves derived experimentally, the author has drawn up a complete equilibrium diagram for gold-lead alloys. In this diagram, the freezing point curve consists of four branches showing three eutectic points at 215° , 254° , and 418° respectively. A consideration of the time required for eutectic crystallisation shows, according to Tammann's method (*Abstr.*, 1904, 113), that there are two definite compounds of gold and lead, namely, AuPb_2 and Au_2Pb ; the occurrence of these compounds was confirmed by a microscopic examination of the alloys. At 211° , there is a polymorphous transformation of the alloy AuPb_2 . This alloy forms brittle, long, white, needle-shaped crystals with rounded contours, and is easily distinguished in appearance from the large, well-formed crystals of the alloy Au_2Pb ; the latter is even more brittle than AuPb_2 .

D. H. J.

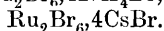
Gold-thallium Alloys. MAX LEVIN (*Zeit. anorg. Chem.*, 1905, 45, 31—38).—Gold and thallium alloys have been studied by the

thermal methods of Tammann with a view to determine the chemical behaviour of the two metals. Cooling curves were made, and an equilibrium diagram constructed; the freezing points of both gold and thallium are lowered by addition of the other metal; the two branches of the freezing point curve intersect at a eutectic point corresponding with a temperature of 131° and with 27 per cent. of gold; there is no evidence of the existence of a definite compound of gold and thallium; this was confirmed by a microscopic examination of the alloys. On the cooling curve of pure thallium, a transformation-point was observed at 225° . From experiments on the velocity of efflux of thallium, Werigin, Lewkoëff, and Tammann (*Ann. Physik.*, 1903, [iv], 10, 647) drew the conclusion that there is a transformation from one crystalline form to another at 180° , hence the possibility of three crystalline modifications of thallium.

D. H. J.

Halogen Compounds of Ruthenium. ALEXANDER GUTBIER and C. TRENNER (*Zeit. anorg. Chem.*, 1905, 45, 166—184).—To obtain the pure metal, the powdered material is heated at a red-heat in oxygen to remove osmium, and the residue (1 part), after reduction with hydrogen, is fused for half an hour with its own weight of potassium nitrate and 8.3 parts of potassium hydroxide; a rapid stream of chlorine is led (at first in the cold, later at 80 — 90°) through an aqueous solution of the product of fusion; the ruthenium tetroxide thus formed is condensed by a freezing mixture of ice and salt and reduced with alcohol; the metal is finally heated in hydrogen.

All attempts to prepare the ruthenious chloride, RuCl_2 , or the ruthenium tetrachloride, RuCl_4 , described by Claus were unsuccessful, nor could a ruthenious bromide be obtained. *Ruthenium sesquichloride*, Ru_2Cl_6 , is obtained either by Claus' method or by evaporating the tetroxide with strong hydrochloric acid; the aqueous solution of the chloride decomposes easily on heating, even at 50° , into a hydrated oxide and hydrogen chloride. The double salts, $\text{Ru}_2\text{Cl}_6 \cdot 4\text{RbCl}$ (dark brown crystals) and $\text{Ru}_2\text{Cl}_6 \cdot 4\text{CsCl}$ (reddish-brown crystals), were prepared. *Ruthenium sesquibromide*, Ru_2Br_6 , is best obtained in a similar way to the chloride; it forms dark scales. The following double salts were prepared: $\text{Ru}_2\text{Br}_6 \cdot 4\text{KBr}$, $\text{Ru}_2\text{Br}_6 \cdot 4\text{NH}_4\text{Br}$, $\text{Ru}_2\text{Br}_6 \cdot 4\text{RbBr}$,



Ruthenium sesqui-iodide, Ru_2I_6 , is obtained as an amorphous, dark-coloured precipitate by heating a solution of ruthenium chloride with potassium iodide solution. The *ammonia compounds*, $\text{Ru}_2\text{Br}_6 \cdot 7\text{NH}_3$ and $\text{Ru}_2\text{I}_6 \cdot 7\text{NH}_3$, corresponding with Joly's compound, $\text{Ru}_2\text{Cl}_6 \cdot 7\text{NH}_3$, are obtained by the action of dry ammonia on the haloid salts; they are insoluble in alcohol.

D. H. J.

Mineralogical Chemistry.

[Analysis of Dognácskaite.] ANTON OTTO (*Tsch. Min. Mitth.*, 1905, 24, 117—118).—The original analysis, by Maderspach (1884), of the incompletely described mineral dognácskaite is quoted below (I): a new analysis gave the results under II.

	S.	Bi.	Cu.	Fe ₂ O ₃ .
I.	15·75	71·79	12·23	—
II.	18·9	42·2	36·1	1·4

The new results agree with the wittichenite formula $\text{Bi}_2\text{S}_3, 3\text{Cu}_2\text{S}$. Dognácskaite is thus possibly identical with wittichenite, although the former has a distinct cleavage, whilst the latter has none.

L. J. S.

Basic Magnesium Carbonates from the Volcanic Eruption at Santorin in 1866. ALFRED LACROIX (*Compt. rend.*, 1905, 140, 1308—1311).—The crusts found on the fumaroles in the lava at Giorgios after the volcanic eruption at Santorin in 1866 were examined by Fouqué and found to consist of sodium chloride with small quantities of sodium sulphate and carbonate and magnesium chloride and carbonate. The author finds that these crusts contain the basic magnesium carbonate, $4\text{MgCO}_3, \text{Mg}(\text{OH})_2, 4\text{H}_2\text{O}$, both in the amorphous condition and in the form of birefringent spherulites, which Fritzsche observed in the artificial carbonate of this composition (*Ann. Phys. Chem.*, 1836, 37, 304). This mineral, which it is proposed to name *giorgiosite*, is regarded as a secondary product formed by the interaction of sodium carbonate with the magnesium chloride associated with the sodium chloride in the crusts. The mineralogical characters of giorgiosite are described briefly in the original.

T. A. H.

Oceanic Salt Deposits. XLII. Formation of Glauberite. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 478—483).—It was sought to determine accurately the temperature of formation of glauberite and to ascertain whether a sodium salt analogous to syngenite is capable of existence. The following transition temperatures were observed in solutions of calcium and sodium sulphates: (1) dehydration of the decahydrated sodium sulphate at $32\cdot4^\circ$; (2) formation of sodium syngenite at $30\cdot2^\circ$; (3) formation of glauberite at 29° . These temperatures would be lowered by the presence of other salts and the values obtained for the three changes are respectively, in the presence of sodium chloride, $17\cdot9^\circ, 15\cdot8^\circ, (14\cdot8^\circ)$; in presence of sodium chloride and glaserite or syngenite, $16\cdot3^\circ, (14\cdot2^\circ), (13^\circ)$; in presence of sodium chloride and blödite, $15\cdot3^\circ, (13\cdot2^\circ), (12^\circ)$; in the presence of sodium chloride, blödite, and glaserite or syngenite, $13\cdot7^\circ, (11\cdot6^\circ), (10\cdot4^\circ)$. The values in brackets are calculated probable values.

L. M. J.

Zeophyllite from Radzein, Bohemia. F. CORNU (*Tsch. Min. Mitth.*, 1905, 24, 127—134).—The recently described mineral zeophyllite (Abstr., 1904, ii, 349) is recorded from a new locality, namely, Radzein, situated between Aussig and Teplitz in Bohemia. It occurs here in an exceptionally fresh leucite-tephrite, associated with apophyllite, calcite, and hyalite, and forms hemispherical aggregates of radially arranged plates with perfect basal cleavage. In its characters, the mineral agrees with the zeophyllite from the original locality (Gross-Priesen); sp. gr. 2.748.

L. J. S.

Physiological Chemistry.

Physicochemical Study of Hæmolysis. Mlle. P. CERNOVODEANU and VICTOR HENRI (*Compt. rend.*, 1905, 140, 1394—1396)—It is found that the rate of hæmolysis of red blood corpuscles in presence of hæmolytic serum varies with the origin of the corpuscles and of the serum. Experiments have been made with corpuscles from the horse, the dog, and the fowl, and with serum extracts from the same animals. The velocity is conditioned by the rate at which the active constituent of the serum is absorbed by the corpuscles, and any change which influences this rate of absorption brings about an alteration in the velocity of hæmolysis. When two different kinds of corpuscles are simultaneously subjected to the action of an active serum, the hæmolysis which takes place in a given time is less than the sum of the effects produced when each kind of corpuscle is separately acted on by the serum under otherwise similar conditions. If two active sera of different origin act simultaneously on one species of corpuscle, the observed effect is much greater than the sum of the effects produced when the two active sera act alone under otherwise similar conditions.

H. M. D.

Hæmolytic Action of Photodynamic Substances. G. SACHAROW and HANS SACHS (*Chem. Centr.*, 1905, i, 1420—1421; from *Münch. med. Woch.*, 52, 297—299). **Action of Light on Mixtures of Blood and Eosin.** **Action of Fluorescent Substances (Eosin) on Normal Serum and Red Blood Corpuscles.** HERMANN PFEIFFER (*Chem. Centr.*, 1905, i, 1421; from *Wien. klin. Woch.*, 18, 221—222, 328—330).—In agreement with Sacharow and H. Sachs, who have worked at the hæmolytic action of various photodynamic materials, but especially with eosin, Pfeiffer finds that light, especially sunlight, causes eosin to act hæmolytically. Eosin does not increase the action of radium bromide. The hæmolysis occurs more readily at elevated temperatures.

Quite minimal additions of eosin (1:2,560,000) to ox-serum and exposure to light destroy the complement and amboceptor; with higher

concentrations, this is more rapid and complete. Agglutinins are more resistant, and precipitogens are unaffected. The photodynamic action is an oxidation process.

W. D. H.

Action of Pepsin. PERCY W. COBB (*Amer. J. Physiol.*, 1905, 13, 448—463).—Using Metts' tubes as a measure of peptic action, it is found that with a tube of 2.5 to 3 mm. bore, digestion is not retarded by the depth of the tube *per se* at depths of less than 7 mm. If 10 c.c. of test solution are employed containing 0.2 per cent. of hydrochloric acid and the tubes are 2 cm. long, a definite decrease in the column digested results from increasing the number of tubes placed in the solution. Making due allowances for these and other errors, pepsin solutions strong enough to digest 4 mm. or more of the columns in twenty-four hours give results far below those anticipated by Schutz' law of square roots. Below this concentration, numbers are obtained in some experiments which approximate to the rule, whilst in other experiments the figures given show no adherence to the law. The divergence is explained by the admixture of inhibitory substances usually present in preparations of pepsin, and often evident in solutions of 1/64 per cent. strength. The "albumin-froth" method of Bettman and Schroeder (*Med. Record, New York*, Oct. 31, 1903) is still less capable of quantitative exactness.

W. D. H.

Starch Digestion in Infants. CYRIL E. CORLETTE (*Australasian Med. Gazette*, 1905, 24, 1—8).—The clinical dictum that starch is an unsuitable food for infants is usually accompanied with instructions for the use of barley water, rice water, arrowroot, &c. Such preparations are starch-containing, and some analyses of the amount present are given. Their administration is not followed by any marked untoward results. A review of previous researches relating to the subject shows that the old idea that infants have no amylolytic ferments is incorrect, and recent work shows the adaptability of the digestive glands to varying forms of diet. At the same time, it should be recognised that there is only one proper and physiologically correct diet for the young infant, namely, its mother's milk.

W. D. H.

End-products of Pancreatic Autolysis. IV. FRIEDRICH KUTSCHER and LOHMANN (*Zeit. physiol. Chem.*, 1905, 44, 381—387. Compare Abstr., 1903, ii, 670, 737; 1904, ii, 425).—Further particulars as to the methods of dealing with the lysine and choline fractions are given. Thymine and uracil were not found.

W. D. H.

The Surviving Intestine. RUDOLF MAGNUS (*Pflüger's Archiv*, 1905, 108, 1—71).—An isolated piece of intestine suspended in oxygenated Ringer's solution continues to show its movements for many hours, and graphic records can be obtained of these by various methods which are described. The action of various drugs can then be studied. Atropine stimulates the movements by acting on Auerbach's plexus, and in large doses stops them in a condition of tonus. Nicotine acts in the contrary way. Muscarine stimulates Auerbach's plexus. Pilocarpine and physostigmine stimulate contraction in the

intestine whether the plexus is present or destroyed. The action of various other agents is also described. W. D. H.

Influence of Sex on the Nutrition of *Bombix mori* in the Last Periods of its Metamorphosis. Localisation of Glycogen, Fat, and Soluble Albumin in the Course of Nymphosis. C. VANEY and F. MAIGNON (*Compt. rend.*, 1905, 140, 1280—1283).—A paper similar in its scope to one already published (this vol., ii, 406). W. D. H.

Distribution of Fat, and the Total Fat in a Fat Dog. K. MOECKEL (*Pflüger's Archiv*, 1905, 108, 189—191).—In a fattened dog, the total fat equalled 25·9 per cent. of its weight. The skin contained 17·9, the subcutaneous tissues 30·1, the muscles 29·9, the viscera *minus* the liver 13·2, the liver 1·1, the bones 7·2, and the brain 0·37 per cent. of the total fat of the body. W. D. H.

Creatine and Creatinine in the Organism. WINCENTY CZERNECKI (*Zeit. physiol. Chem.*, 1905, 44, 294—308).—Instances of methylation in the body are given, and the present research is directed to determining whether guanidine is the parent substance of creatine and creatinine. The experiments consisted in giving glycocyamine (guanidine-acetic acid) to rabbits. This led to an increase of nitrogen in the urine corresponding with 62 per cent. of that in the glycocyamine, and a certain fraction of this increase is in the form of creatinine. Some reappears as glycocyamine. If creatine is given, possibly part is excreted unchanged, but this is difficult to prove with the present means of estimation; a very small part appears as creatinine, and about half as urea. Creatinine itself does not appear to be well absorbed; about half appears as such in the urine, and the amount of urea also rises. Glycocyamine stimulates proteid katabolism; there is no increase in creatinine. W. D. H.

The Value of the Cleavage Products of Casein in the Animal Organism. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1905, 44, 198—205. Compare Abstr., 1904, ii, 749; 1905, ii, 334).—Further experiments in favour of the view that proteid synthesis from simple cleavage products of proteolysis occurs in the body. Free amino-acids when administered do not reappear in the urine. W. D. H.

Formation of Protamines in the Animal Body. ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1905, 44, 347—352).—A contrast is drawn between the different groupings present in various protamines, and this is followed by theoretical deductions as to the way in which the linking may be brought about within the protoplasmic molecules. W. D. H.

Nitrogen Distribution in the Liver of the Sturgeon. ALFRED J. WAKEMAN (*Zeit. physiol. Chem.*, 1905, 44, 341).—The following figures compare the livers of dog and sturgeon:

			Dog.	Sturgeon.
Dry substance per cent.	27.07	28.84
Nitrogen per cent. in dry substance	11.77	7.07

Nitrogen per cent. of total nitrogen :

In arginine	9.32	6.77
In histidine	2.29	1.75
In lysine	4.75	4.05

Quantity of these bases in 100 parts of dry substance :

Arginine	3.40	1.49
Histidine	0.99	0.46
Lysine...	2.90	1.49

W. D. H.

Chemical Changes in Bone Marrow after Intraperitoneal Injection of Bacteria. PAUL TH. MÜLLER (*Beitr. chem. Physiol. Path.*, 1905, 6, 454—480).—The composition of blood-plasma in normal rabbits is moderately constant; the average proteid-quotient (globulin:albumin) is 1:1.42. The injection of different virulent but dead cultures increases the fibrinogen and the total proteid of the blood-plasma; the serum globulin was not much affected. In the bone marrow, the total proteid and the fibrinogen were also much increased, especially by cultures of *Staphylococcus*. The fibrinogen in this situation is so great that mere admixture with blood and lymph will not account for it all; its origin is believed to be in the marrow.

W. D. H.

Action of Acids and Alkalis on the Staining Reactions of Animal Tissues. ALBRECHT BETHE (*Beitr. chem. Physiol. Path.*, 1905, 6, 399—425).—A description, mainly histological, of the action of various dyes such as toluidine-blue on different tissues, and the varying intensity of the coloration when measured amounts of acid and alkali are added. The main results are represented by curves, and no general rule for different tissues appears possible. Nuclei and Nissl's granules are stainable in the presence of excess of hydrogen ions; nerve fibres only in neutral solutions of such a dye as thiazine zinc-chloride; that is, in the absence of free hydrogen ions, they can liberate the base from the compound. Glia tissue among others is not able to do so even in neutral solutions. A discussion on the theories of staining concludes the paper.

W. D. H.

Fat in Human Milk. RODOLPHE ENGEL (*Zeit. physiol. Chem.*, 1905, 44, 353—365).—The iodine number differs greatly in the milk of different women, and in individual women is subject to daily variations.

W. D. H.

Oxidation by the Urine. K. BERTRAM (*Pflüger's Archiv*, 1905, 108, 109—114).—If a little indigo is added to urine, and then ferrous

sulphate, the indigo is destroyed. If distilled water is used instead of urine, this does not occur. The oxidising action of the urine can also be demonstrated on arsenious acid and other substances, and can be determined quantitatively. It is attributed to the presence of hydrogen peroxide.

W. D. H.

Iron in Diabetic Urine. S. ZUCCHI (*Zeit. physiol. Chem.*, 1905, 44, 171—172).—Neumann and Mayer have described four cases of diabetes in which there was a constant relation between the sugar and the iron in the urine. This is important in view of the possible origin of sugar from nucleic acid. Three cases are, however, now recorded in which the proportion varied from 1·7 to 3·4 mg. iron per 100 grams of sugar.

W. D. H.

Sugar in the Blood during Parturition in the Goat deprived of its Mammary Glands. CH. PORCHER (*Compt. rend.*, 1905, 140, 1279—1280).—Glycosuria and glycaemia occur in the pregnant goat if the operation of ablation of the mammae has been performed. In ordinary circumstances, the sugar would no doubt have been secreted as lactose in the milk. The glycosuria, however, is not detected until delivery takes place, and disappears a few days later.

W. D. H.

Ether-glycosuria, and the Effect of Intravenous Oxygen Infusion on it. ALBERT SEELIG (*Chem. Centr.*, 1905, i, 1330—1331; from *Arch. exp. Path. Pharm.*, 52, 481—494).—Ether inhalations in dogs produce transient glycosuria, which is hindered by carbohydrate feeding. The glycosuria is accompanied by glycaemia and a diminution of the hepatic glycogen. Simultaneous administration of oxygen intravenously prevents the glycosuria.

W. D. H.

Origin of the Sugar excreted in Pancreatic Diabetes. EDUARD PFLÜGER (*Pflüger's Archiv*, 1905, 108, 115—188)—As an exclusively proteid diet for dogs, codfish was chosen; when boiled, it is free in winter and spring from glycogen and glucosides, and contains only traces of fat. Dogs without a pancreas so fed secrete in a month 30 per cent. of their body weight of sugar, or a weight greater than all the proteid of their body. The sugar must originate either from the fat or proteid of the body or of the food. In spite of the food, the body wastes "to a skeleton," only heart and brain remaining unaffected. The liver enlarges enormously to 5 per cent. of the body weight, or five times more than in ordinary starvation; it is normal in composition. In diabetics the liver is always richest in fat. There is no constant proportion between the sugar and nitrogen of the urine, and so the origin of sugar from proteid is doubted. The sugar is believed to originate in the liver cells, which are capable of turning fat as well as glycogen into sugar. The liver overgrows owing to the large amount of work it has to do in relation to proteid ingested; its sugar-forming function is simultaneously increased. Any stimulus of the liver such as ammonium carbonate or neutral soaps increases the sugar formed.

W. D. H.

Urine in Phosphorus Poisoning. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1905, **44**, 428. Compare Abstr., this vol., ii, 338).—A supplementary note discussing the composition of arginine picrolonate, the form in which arginine was separated from the urine.

W. D. H.

Chemical Changes in the Liver in Phosphorus Poisoning. ALFRED J. WAKEMAN (*Zeit. physiol. Chem.*, 1905, **44**, 335—340).—In phosphorus poisoning, the percentage of nitrogen in the liver substance diminishes. The amount of arginine, histidine, and lysine obtained is lessened, and is small in proportion to the total nitrogen. W. D. H.

The Liver in Phosphorus Poisoning. J. MEINERTZ (*Zeit. physiol. Chem.*, 1905, **44**, 371—379).—According to Waldvogel (*Centr. Stoffwechsel- u. Verdauungskrankheit*, 1903, 405), protagon is present in large amounts among the fats in the livers of cases of phosphorus poisoning. In the present research on dogs, this was not confirmed; similarly, doubt is cast on estimations of jecorin.

W. D. H.

Excretion of β -Naphthol in the Urine after the Administration of Small Doses of Naphthalene, Benzo-naphthol, and β -Naphthol. G. EDLEFSEN (*Chem. Centr.*, 1905, i, 1341; from *Arch. exp. Path. Pharm.*, **52**, 429—458).—The β -naphthol which appears in the urine after the administration of naphthalene is mainly combined with glycuronic acid, and to a less degree as an ethereal sulphate. After the administration of benzo-naphthol [β -naphthyl benzoate], it is wholly excreted as ethereal sulphate; after the administration of β -naphthol mainly as ethereal sulphate. β -Naphtholglycuronic acid is detected (1) by the red colour given by glacial acetic acid and sodium nitrite, (2) by the occurrence of β -naphthaquinone after treatment of the urine with hydrochloric acid and calcium chloride, and (3) by the blue fluorescence produced by adding ammonia or potassium hydroxide.

W. D. H.

Indole and Scatole in the Organism. PAUL GROSSER (*Zeit. physiol. Chem.*, 1905, **44**, 320—334).—In dogs, Wang found that after administration of indole it reappears in the urine within 24 hours, partly as ethereal sulphates, partly as an indigo-forming substance. The present research relates to rabbits; normally their urine does not contain an indigo-forming substance; if indole is given, it is completely excreted within 48 hours; less ethereal sulphate appears than corresponds with the indole given; after feeding, about 16 per cent. reappears as indigo-forming substance; this rises to 30 per cent. after subcutaneous injection. After scatole, there is a rise in the ethereal sulphate excretion, but the general quantitative results are not so satisfactory. Some work was done in regard to the scatole pigments in the urine; one is soluble only in alcohol, another in both alcohol and acetone; the former shows the same absorption bands as urorosein.

W. D. H.

Toxicity of Urinary Alkaloids. H. GUILLEMARD and P. VRANCEANO (*Compt. rend.*, 1905, **140**, 1277—1279).—Under normal conditions, the alkaloidal toxicity varies between 18 and 25 per cent. of

the "globale" toxicity of the urine. It is not proportional to the quantity of alkaloids, but depends on their nature. Creatinine is only slightly poisonous. Silico-tungstic acid is recommended as a suitable reagent for precipitating some of the urinary alkaloids. W. D. H.

Selective Action of Chloroform on the Liver. MAURICE DOYON and J. BILLET (*Compt. rend.*, 1905, 140, 1276—1277).—In certain circumstances, chloroform causes uncoagulability of the blood and disappearance of fibrinogen; this is attributed to injury of the liver. The present paper deals with the liver lesions, which are principally hæmorrhages, accumulation of polynuclear leucocytes, and hyaline degeneration of the cells. No other organ is affected except the kidney, which exhibits acute inflammation. The chloroform was administered by the stomach sound to dogs in doses of 2 grams daily per kilo. of body weight. Death usually occurs on the third day. W. D. H.

Action of Alcohol on the Heart of Warm-blooded Animals. OSWALD LOEB (*Chem. Centr.*, 1905, i, 1331; from *Arch. exp. Path. Pharm.*, 52, 459—480).—In weak concentration, alcohol causes sometimes a slight stimulating action on the heart; in a concentration of more than 1 per cent. its action is the reverse, culminating in stoppage. W. D. H.

Physiological Behaviour of Methylene-blue and Methylene-azure. FRANK P. UNDERHILL and OLIVER E. CLOSSON (*Amer. J. Physiol.*, 1905, 13, 358—371).—The evidence is insufficient that a conjugate substance is formed in the organism after the introduction of methylene-blue. The facts can be explained by the presence of two leuco-compounds or chromogens corresponding with methylene-blue and methylene-azure respectively. If pure methylene blue is introduced intravenously, intraperitoneally, or by the mouth, the following substances appear in urine and fæces: methylene-blue, methylene-azure (an oxidation product of methylene-blue), and the two chromogenic substances. If pure methylene-azure is injected, only a portion is regained, partly as such, partly as its leuco-compound. Small doses of either the blue or the azure fail to appear in the urine; it is only when oxidation is inadequate in the organism that they are manifested. The experiments were made on dogs and rabbits, and demonstrate the simultaneous action of both oxidation and reduction in the organism. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Physiological Action of Ozone. WILHELM SIGMUND (*Centr. Bakt. Par.*, 1905, 14, 400—415).—Two essential points in the method adopted are: (1) the ozone was prepared free from impurities; (2) the percentage of ozone mixed with air or oxygen was quantitatively determined. Quite small admixtures with ozone weaken or destroy the action of various enzymes and micro-organisms. W. D. H.

Decomposition of Fodder and Foods by Micro-organisms.
V. Composition of the Products formed by the Bacteria. JOSEF KÖNIG, ALB. SPIECKERMANN, and FR. SEILER (*Zeit. Nahr. Genussm.*, 1905, 9, 513—528. Abstr., 1903, ii, 169, 447).—The decomposition products (slimes) examined were found to be produced by many species of bacteria not only from foods containing sugar, but also from those containing nitrogenous substances such as peptone, asparagine, and glycine. The products formed from both liquid and solid media always consisted largely, if not entirely, of anhydrides of carbohydrates. These anhydrides belonged to the levulose and dextrose groups, and also to the galactose group. Dextran could not be detected. W. P. S.

Bacteriological and Chemical Study of the Fermentation of Red Beet, known as "Barszcz." KAZIMIERZ PANEK (*Bull. Acad. Sci. Cracow*, 1905, 5—49).—"Barszcz" is a fermentation caused by *Bacterium betaë viscosum* in red beet at a temperature of 18—20°. It goes on at the expense of the sucrose present in the roots, and results in the production of dextran, mannitol, acetic and lactic acids. Ester-producing bacteria have a share in the process at the commencement of the fermentation. N. H. J. M.

The Large Bacillus observed in Flacherie. S. SAWAMURA (*Bul. Coll. Agr. Tōkyō*, 1905, 6, 375—386).—A large bacillus, *Bacillus megatherium bombycis*, was obtained from newly-hatched silkworms and from the excreta of a young larva. The bacillus is very widely distributed, and occurs in the digestive canal of healthy insects without injuring them. When cultivated on solid media and given to silkworms, death of the latter soon follows.

Flacherie is caused by several bacteria which occur commonly on mulberry leaves. N. H. J. M.

Effect of Various Carbohydrates and Organic Acids on the Metamorphosis of Nitrates by Bacteria. JULIUS STOKLASA and E. VÍTEK (*Centr. Bakt. Par.*, 1905, ii, 14, 493. Compare this vol., ii, 342).—Cultures of *Bacillus Hartlebi* yielded the enzyme which gives rise to a lactic acid and alcoholic fermentation in dextrose, levulose, sucrose, and maltose. The process goes on in presence of oxygen, as previously indicated, acetic and formic acids being produced. In absence of sodium nitrate, carbon dioxide and hydrogen are evolved, whilst when nitrate is present the hydrogen is partially oxidised to water, so that the mixture of gases consists of nitrogen, carbon dioxide, and hydrogen. N. H. J. M.

A Case of Bacterial Deposition of Iron in a Water Supply. ADOLF BEYTHIEN (*Zeit. Nahr. Genussm.*, 1905, 9, 529—531).—The water supply of a small town in Saxony after passing through two kilometres of iron mains was found to contain a considerable quantity of ferruginous suspended matter, although, when drawn from the spring, the water contained no iron. A microscopical examination showed that the suspended matter consisted of a mass of threads, similar to *Crenothrix*, which were incrustated with iron oxide. These threads were in all probability *Gallionella ferruginea*, and the contamination of the supply was due to their presence, and also to the large amount of free carbon dioxide dissolved in the water. W. P. S.

The Decomposition Phases of Milk. C. J. KONING (*Milchw. Zentr.*, 1905, 1, 215—229).—The spontaneous decomposition of milk may be divided into eight phases or periods, in each of which one or more species of bacteria have their maximum activity. In each locality, the decomposition is governed by the bacterial flora there present. The acidity of the milk stands in relation to the activity of specific bacteria. The fungi, strictly speaking, alter the reaction of the decomposed milk, and give to certain bacteria, the functions of which have ceased, a further period of activity. In Holland, where this investigation was carried out, the lactic acid fermentation was found to be due to the growth of *Streptococcus acidilactici* Grotenfelt, *B. acidilactici* Hueppe, *B. acidiparalactici* Kozai, and *B. acidilactici* Grotenfelt, and the butyric acid fermentation to *Granulobacillus saccharobutyricus immobilis liquefaciens* Schattenfroh and Grassberger.

W. P. S.

Some New Varieties of Mycoderma Yeast. T. TAKAHASHI (*Bul. Coll. Agric. Tôkyô*, 1905, 6, 387—401).—Four varieties were obtained which have the property of assimilating some nitrogen from nitrites when glycerol is supplied as the source of carbon. This has not been previously observed, Beijerinck's *Saccharomycetes acetathylicus* only assimilating nitrogen as nitrates. Six varieties (including two of the above) grew in saké containing 10·77 or 13·32 per cent. of alcohol.

Most of the varieties isolated produced a distinct trace of methyl alcohol, in addition to ethyl alcohol, from kôji extract. All produced acetic acid from alcohol, and some also from glycerol. Some formed butyric acid as well as acetic acid, and a few formic acid in saccharine solutions.

N. H. J. M.

Plasmolysis and Turgor-regulation of Pressed Yeast. N. H. SWELLENGREBEL (*Centr. Bakt. Par.*, 1905, ii, 14, 374—388 and 481—492).—The loss of glycogen, during anatonose, in cells rich in glycogen and the dying off of cells which retain glycogen support the view that yeast can regulate its turgor by decomposition of glycogen. On the other hand, cells deficient in glycogen regulate their turgor just as quickly as those containing an abundance of glycogen.

N. H. J. M.

Further Researches on Cell-free Fermentation. EDUARD BUCHNER and WILHELM ANTONI (*Zeit. physiol. Chem.*, 1905, 44, 206—228).—Expressed yeast juice loses its fermentative action by

exposure to the air. This was attributed to the destruction of zymase by atmospheric oxygen before it was found to be produced by the proteolytic enzyme of the juice. Certainly the presence of hydrogen instead of oxygen makes no difference in the result. Attempts to separate the zymase from the invertase of the juice by dialysis and by fractional precipitation with alcohol failed. In highly concentrated solutions of sucrose (70 per cent.), both ferments are effective. The inhibitory influence of formaldehyde, sodium fluoride, alcohol, and acetone is described with quantitative tables. Acetone is more harmful than alcohol. The favourable influence of extremely small quantities of quinine hydrochloride (described by Grigorieff) is very slight, and is perhaps due to its harmful influence on the proteolytic ferment.

W. D. H.

Contribution to the Biochemistry of Sewage Purification; the Bacteriolysis of Peptones and Nitrates. STEPHEN DE M. GAGE (*J. Amer. Chem. Soc.*, 1905, 27, 327—363).—Bacteria commonly occur in sewage purification, which produce ammonia and free nitrogen from organic matter, reduce nitrates, and fix free nitrogen. Probably there are also bacteria present which produce lower oxides of nitrogen. The amount of ammonia produced may be as much as 180 per million. The rate of the different actions may vary very considerably. Some cultures reduce nitrates to nitrites, ammonia, and free nitrogen continuously from the commencement; in others, the reductions occur consecutively. In some instances, the production of nitrites is greater than the amount of nitrates, indicating that oxidation is going on at the same time.

Most of the cultures reduce nitrates and produce ammonia from peptone. Many non-liquefying bacteria reduce nitrates and produce ammonia from peptone; and many liquefying bacteria exist which do not possess these functions.

N. H. J. M.

Influence of Radium on the Respiratory Energy of Germinating Grains. H. MICHEELS and P. DE HEEN (*Acad. Roy. Belg.*, 1905, 29—34).—See this vol., ii, 431.

Peptone in Seeds. WILHELM ROBERT MACK (*Bied. Centr.*, 1905, 34, 226—229; from *Inaug. Diss. Leipzig*, 1903. Compare *Abstr.*, 1904, ii, 762).—Resting seeds of lupins contain considerable amounts of peptone. The vegetable peptone resembles Siegfried's peptonic acids. It is a dibasic acid having a characteristic barium salt.

N. H. J. M.

Action of Ethyl Ether and Chloroform on Dry Seeds. PAUL BECQUEREL (*Compt. rend.*, 1905, 140, 1049—1052).—Entire seeds which were kept a year in chloroform or ethyl ether retained their germinating power, whilst seeds the tegument of which had been perforated or partially removed were destroyed. Both substances dissolved the fatty substances of the cell, but chloroform produced further changes extending to the proteids.

N. H. J. M.

Chemotropism of the Root. MAURICE LILIENFELD (*Chem. Centr.*, 1905, i, 1328—1329; from *Ber. deut. bot. Ges.*, 23, 90—96).—The rootlets of lupin seedlings were allowed to grow into gelatin, to which various substances were added; positive curvatures were produced by

disodium hydrogen phosphate, ammonium phosphate, potassium carbonate, and potassium dihydrogen phosphate; negative curvatures by sodium chloride, magnesium sulphate, ferric nitrate, aluminium nitrate, copper sulphate, copper chloride, zinc sulphate, lead nitrate, mercuric nitrate, and mercuric chloride. Potassium carbonate and nitrate are either indifferent or partly positive. W. D. H.

Chlorophyllous Assimilation in Young Shoots of Plants. Application to the Vine. ED. GRIFFON (*Compt. rend.*, 1905, 140, 1148—1151).—Experiments with young leaves attached to stems showed that assimilation may be very feeble, and is easily masked by respiration.

Young leaves, especially of vine, were found to be free from starch. The parasitism of the tops of vines is very feeble when it exists at all, which is not the case when one or two well-developed leaves are present. N. H. J. M.

Composition of Solid Fats of Plants. ISIDOR KLIMONT (*Monatsh.*, 1905, 26, 563—569. Compare Abstr., 1901, i, 663; 1902, i, 340; 1903, i, 731; this vol., ii, 126).—Oleodistearin (Henriques and Künne, Abstr., 1899, i, 330) has now been found in *oleum stillingiae* and in cacao fat, which melts at 32·5° and has an acid number 1·7, an iodine number 35·4, and a saponification number 196·5.

Oleodipalmitin, obtained from cacao fat, from *oleum stillingiae*, or from Borneo tallow, melts at 38° (m. p. 33—34°; this vol., ii, 126).

All the glycerides found in vegetable fats are hydrolysed with relative difficulty, and are stable towards atmospheric action.

G. Y.

Formation and Rôle of Fatty Substances in Fungi. A. PERRIER (*Compt. rend.*, 1905, 140, 1052—1054).—Experiments with different fungi showed that the fatty substances increase from the commencement and may amount to 30 per cent. or more of the dry matter. The amount remains about constant in presence of an excess of nutritive substances, but diminishes when these are deficient.

N. H. J. M.

Chrysanthemums. II. ALEXANDRE HÉBERT and GEORGES TRUFFAUT (*Bull. Soc. chim.*, 1905, [iii], 33, 661—664. Compare Abstr., 1903, ii, 608; 1904, ii, 140).—From analyses of the mineral constituents of chrysanthemums made when the flower-buds first appear, towards the end of July, and when the first flowers open, early in October, it is found that far more mineral matter is absorbed by the plant during the last 64 days of growth than during the first 178 days. During the first period, chrysanthemums absorb from the soil 1·42 units of potash and 0·28 units of phosphoric acid for each unit of nitrogen, and during the second period 1·23 units of potash and 0·47 units of phosphoric acid for each unit of nitrogen. This indicates that manures should be applied at the end of August, and that they should contain the three essential constituents in the above proportions.

T. A. H.

Chlorosis of Plants. A. DOMENTÉEFF (*Bied. Centr.*, 1905, 34, 185—186; from *J. exper. Landw.*, 1903, 4, 733).—Chlorose is attributed to an excess of salts in the leaves caused by injury to the roots by parasites or by digging the surrounding soil. The accumulated mineral matter closes the pores of the leaves and hinders the production of chlorophyll, whilst the chlorophyll already formed is destroyed by the action of light.
N. H. J. M.

Physiological Effects of Ozone. WILHELM SIGMUND (*Centr. Bakt. Par.*, 1905, ii, 14, 494—502).—Ozone retards the curdling of milk, but not sufficiently to be of use as a preservative. The employment of larger amounts of ozone would cause alterations in the composition of the milk. The rapid curdling of milk during thunderstorms cannot be due to ozone, and is undoubtedly due in part to the higher temperature which prevails. It is suggested that the nitrous acid and oxides of nitrogen produced in storms may have something to do with it.

Mycoides and nodule-bacteria, when ozonised for an hour (with 1.2 mg. O_3), were not killed, but their development was retarded.

Small amounts of ozone were found to be beneficial to the germination of peas, whilst larger amounts were injurious.

N. H. J. M.

The Reactions of Living Cells to Very Dilute Solutions of Various Substances. THOMAS BOKORNY (*Pflüger's Archiv*, 1905, 108, 216—236).—Solutions of various substances were made of 0.1 per cent. strength; this was diluted down 10, 100, 1000, &c., fold, and one of the remarkable points brought out is the intensely poisonous action of the materials used on animal and vegetable cells; the more dilute the solution, the longer is the time required for this to manifest itself. In some cases (mercuric chloride, copper sulphate, and other salts of heavy metals), this is attributed to compounds which are formed between the poisons and the proteid matter of the protoplasm. In others (ammonia, caffeine, and other organic bases), the poisons act as stimuli, the histological sign of which is "aggregation" of particles in the protoplasm.
W. D. H.

Effect of Rust on the Straw and Grain of Wheat. FRANK T. SHUTT (*J. Amer. Chem. Soc.*, 1905, 27, 366—369).—Rusted straw contains increased percentages of crude proteid and fat. In rusted grain, the proteids are 3.19 per cent. higher than in normal grain; the fibre and ash are also higher, whilst water, carbohydrates, and fat are lower.

Whilst rust results in the production of a more nitrogenous grain, it also considerably reduces the total yield. In the present case, the yield was reduced by about 50 per cent. The proportion of flour to bran is also reduced, presumably.
N. H. J. M.

Influence of Stimulants on the Consumption of Food. Digestibility and Secretion of Milk with Non-stimulating and Normal Food. GUSTAV FINGERLING (*Landw. Versuchs-Stat.*, 1905, 62, 11—180).—When added to a food entirely free from stimulant,

the effect of stimulants is to increase the consumption of food and the yield of milk and milk constituents. When, however, stimulants are added to a normal food (which contains stimulating substances), no effect is produced.

In practice, the use of stimulants is only of use in exceptional cases, such as, for instance, when cattle are fed with hay damaged by rain. In such cases, addition of fenugreek, anise, or caraway seed is recommended (compare J. B. Lawes, *Edinb. Vet. Rev.*, 1862; *Rothamsted Memoirs*, 2, No. 16).
N. H. J. M.

Composition of Milan Milk. C. BERTOCCHI (*Milchw. Zentr.*, 1905, 1, 211—215).—Further results are given showing the composition of the milk of Milan and surrounding districts (Abstr., 1905, ii, 361). The milks contained frequently less than 12 per cent. of total solids, the minimum quantity found being 11·6 per cent. The lowest percentage of non-fatty solids observed was 8·08. W. P. S.

Experiments on the Accumulation and Utilisation of Atmospheric Nitrogen in the Soil. EDWARD B. VOORHEES and JACOB G. LIPMAN (*J. Amer. Chem. Soc.*, 1905, 27, 556—589).—Experiments were made in boxes with cow-peas without nitrogen and with different nitrogenous manures. The cow-peas were followed by two crops of millet.

The results showed that the soils gained nitrogen during the growth of cow-peas, and there are indications that fixation of nitrogen in the soil continued after the removal of the cow-peas. In soils supplied with organic matter, there was considerable fixation of nitrogen; soils, however, with which large amounts of a leguminous crop were incorporated did not show a gain of nitrogen. The conclusion is drawn that non-symbiotic fixation of nitrogen is most active in open soils with fairly large amounts of organic matter having a low percentage of nitrogen.
N. H. J. M.

Preservation and Action of the Nitrogen of Urine. E. BÖHME (*Bied. Centr.*, 1905, 34, 300—304; from *Illust. landw. Zeit.*, 1904, 24).—Gypsum (10 per cent.) reduced the loss of nitrogen to 7 per cent. in 250 days, urine alone losing 56 per cent. of its nitrogen in the same time. Sulphuric acid (1 per cent.) reduced the loss to 5·5 per cent., whilst with 2 per cent. of sulphuric acid the whole of the nitrogen was retained.

The results of manurial experiments showed that addition of lime and gypsum increased the action of urine, and that in presence of these substances and sulphuric acid the nitrogen of urine had better effects when applied before the seed than as top-dressing,

The nitrogen of urine is almost equal in value to that of sodium nitrate.
N. H. J. M.

Action of Calcium Cyanamide. WILLY ZIELSTORFF (*Bied. Centr.*, 1905, 34, 217—218; from *Illust. landw. Zeit.*, 1904, 24, 1103).—The results of pot experiments with mustard showed that when calcium cyanamide was applied at the same time as the seed its value was 88·4 per cent.

of that of sodium nitrate. When the seed was sown 10 days after the application of the manure, the value of the latter increased to 92·8 per cent. Ammonium salts give less favourable results.

Results obtained with a second crop showed that calcium cyanamide had no appreciable after effect. The manure should not be applied as a top-dressing.

N. H. J. M.

Fruit Tree Manures. H. CLAUSEN (*Bied. Centr.*, 1905, **34**, 219—221; from *Landw. Jahrb.*, **33**, 939—960).—Kainite and basic slag (1 kilo. per tree) applied in April injured apple trees, the injurious effects lasting for three years. Marl had a beneficial effect and in many cases diminished injury due to kainite and basic slag. Nitrogenous manures promote the formation of wood, whilst the exclusive use of mineral manures restricts wood-production. Ammonium sulphate proved to be beneficial and much preferable to sodium nitrate.

N. H. J. M.

Calcium Nitrate in Agriculture. E. S. BELLENOUX (*Compt. rend.*, 1905, **140**, 1190).—Potatoes manured with calcium nitrate produced tubers containing 1·8 per cent. more starch than those manured with sodium nitrate. Similar experiments with sugar-beet showed an increase of 1·37 per cent. of sugar with calcium as compared with sodium nitrate.

The calcium nitrate was prepared by the action of sodium nitrate on calcium chloride, the sodium chloride produced separating during the concentration.

N. H. J. M.

Analytical Chemistry.

New Apparatus for Gas Analysis. GINO POLLACCI (*Ann. Chim. anal.*, 1905, 10, 169—170).—A rather complex apparatus for gas analysis, suitable for the analysis of the gases obtained in experiments on vegetation ; for the details, the original must be consulted.

L. DE K.

New Method for the Estimation of Mixtures of Chlorides, Iodides, and Bromides. O. WENTZKI (*Zeit. angew. Chem.*, 1905, 18, 696—698).—A modification of the well-known indirect silver process based on the fact noticed by the author that iodides and bromides are converted into chlorides by adding excess of mercurous chloride and also that an iodide is converted into bromide by means of mercurous bromide.

In the case of a mixed chloride and iodide, a portion of the liquid is precipitated with silver nitrate and the precipitate is collected and weighed as usual ($\text{AgCl} + \text{AgI}$). An equal volume of the liquid which has been shaken with a large excess of precipitated mercurous chloride

is then also precipitated (AgCl). From the two weights obtained, the result may be calculated in the well-known manner. Chlorides and bromides are treated in the same manner, the respective precipitates being $\text{AgBr} + \text{AgCl}$ and AgCl . In the case of a bromide and iodide, mercurous bromide is employed, the respective precipitates being $\text{AgBr} + \text{AgI}$ and AgBr . In case all three halogens are present, one portion is precipitated directly, a second portion after treatment with mercurous chloride, and a third after treatment with mercurous bromide, the results being respectively $\text{AgCl} + \text{AgBr} + \text{AgI}$, $\text{AgCl} + \text{AgBr}$, and AgCl .

L. DE K.

Estimation of Oxygen in Copper. S. DICKSON (*Analyst*, 1905, 30, 145—147).—Ten grams of the copper, in one piece, and 20 grams of tin (previously fused in an atmosphere of hydrogen) are placed in a boat and heated in a porcelain tube until complete fusion has taken place, dry hydrogen being passed through the apparatus. The water formed is caught in an ordinary sulphuric acid U-tube. The results obtained are usually slightly higher than those yielded when the copper itself is fused without the addition of tin.

W. P. S.

Iodometric Estimation of Sulphurous Acid. ERWIN RUPP (*Ber.*, 1905, 38, 1903—1905. Compare *Abstr.*, 1903, ii, 40).—In reply to Ruff and Jeroch's criticisms (this vol., ii, 200), it is pointed out that whereas these authors added the iodine solution to the sulphurous acid solution containing sodium hydrogen carbonate, Rupp added the sulphite solution to the iodine solution containing sodium hydrogen carbonate. Under the later conditions, neither the oxidising influence of the air nor the formation of sodium hypiodite introduces an error, and the method gives satisfactory results.

E. F. A.

Detection of Free Yellow Phosphorus in Phosphorus Sulphide. LÉO VIGNON (*Compt. rend.*, 1905, 140, 1449—1451).—The presence of free yellow phosphorus in commercial phosphorus sulphide cannot be readily detected by the ordinary methods; Mitscherlich's test fails because the pure sulphide P_4S_3 is partially decomposed when distilled with water; also the pure sulphide and the commercial compound each boil at 250 — 254° under 30 mm. pressure, whilst mixtures of the pure sulphide with 2.64 or 1.80 per cent. of yellow phosphorus boil at 160 — 260° and 250° respectively; if, however, a current of pure hydrogen is passed over the suspected compound, the issuing gas is luminous and burns with a green flame in the presence of free yellow phosphorus.

M. A. W.

Estimation of Phosphoric Acid by the Citrate Method; a Source of Error hitherto overlooked and a Modification for avoiding it. VINCENT SCHENKE (*Landw. Versuchs-Stat.*, 1905, 62, 3—10).—In the usual citrate method, 50 c.c. of the acid phosphate solution (= 0.5 gram of substance) are treated with 100 c.c. of citrate solution and 25 c.c. of magnesia mixture. The following modification is proposed. The solution (50 c.c.) is nearly neutralised with ammonia, quickly cooled, and treated with 50 c.c. of citrate solution and 25 c.c.

of magnesia mixture. It is then stirred for half an hour and filtered after several hours. A number of results are given showing close agreement with the molybdate method (Maercker), whilst the method of the German Association gave, in every case, lower results, owing to the greater solubility of the magnesium ammonium phosphate in the citrate solution, which had been altered from that originally proposed by the addition of a considerable amount of acid. N. H. J. M.

Separation of Arsenic. H. CANTONI and J. CHAUTEWS (*Arch. Sci. phys. nat.*, 1905, [iv], 19, (4), 364—366).—When a current of air is passed through a hydrochloric acid solution of arsenic trioxide containing methyl alcohol, the arsenic is completely removed at the ordinary temperature in the form of its methyl ester, whilst antimony compounds are not volatile under these conditions. M. A. W.

Detection of Boric Acid [in Foods]. O. VON SPINDLER (*Chem. Zeit.*, 1905, 29, 566—567).—Boric acid may be detected by the turmeric reaction if care is taken to use properly prepared turmeric paper. The flame reaction as usually applied is less trustworthy, even if methyl alcohol is substituted for ethyl alcohol. The following modification of the flame test gives satisfactory results.

Five to ten grams of the comminuted substance are rubbed in a mortar with 5 drops of dilute sulphuric acid (1 : 4) and introduced into a flask containing 30—40 c.c. of strong methyl alcohol. The flask is heated in a water-bath at 70—75° and a current of coal gas is passed through. If this should now burn with a green flame, boric acid is undoubtedly present. L. DE K.

Electrical Method for the Combustion of Organic Compounds. HARMON N. MORSE and L. S. TAYLOR (*Amer. Chem. J.*, 1905, 33, 591—603).—An electrical method is described for the estimation of carbon and hydrogen in organic compounds which is said to have the following advantages. The apparatus is small and compact, the waste of heat energy is much smaller than that of the ordinary method, and the time required in preparing for and carrying out a combustion is considerably reduced.

Two forms of apparatus are described. The first of these consists of a thin glass combustion tube, 350 mm. long, 15 mm. in internal diameter, and closed at one end. The open end is fitted with a caoutchouc stopper through which pass a porcelain tube, 250 mm. long and 6 mm. in diameter, a glass tube conveying the products of combustion to the absorption apparatus, and a thick platinum wire. The platinum wire is connected inside the combustion tube to a finer platinum wire which surrounds the porcelain tube in a spiral coil and finally passes down through the porcelain tube to the exterior, the lower part being composed of thicker wire. The oxygen or air is led into the combustion tube through a glass side-tube, which is attached to the porcelain tube outside the stopper by means of india-rubber tubing.

In carrying out a combustion, the boat containing the substance is placed at the closed end of the tube, a roll of copper gauze about

60 mm. long is placed next, the india-rubber stopper carrying the tubes and platinum wire is inserted, and the glass delivery tube is attached to the absorption apparatus. Pure dry oxygen is passed slowly through the tube and the electric circuit is closed through a regulating rheostat. The current is increased until the wire becomes red-hot, and the roll of copper gauze and the boat containing the substance are then heated by means of a gas flame. The time required for a combustion is usually about half an hour. The amount of electrical energy consumed is about 3.6 amperes at 54 volts during the time when the highest temperature is maintained.

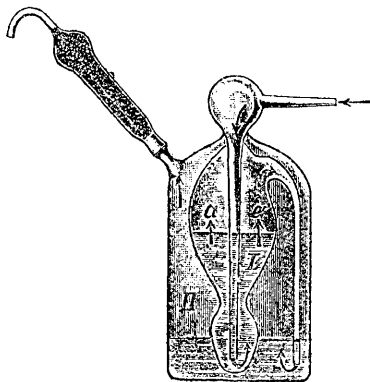
The second form of apparatus described differs in being composed of a somewhat longer combustion tube which is open at both ends. Both forms of apparatus are fully described with the aid of diagrams.

The results of a series of combustions are quoted for the purpose of illustrating the applicability and accuracy of the method, and an account is given of the precautions which must be observed in the combustion of substances containing nitrogen, halogens, or sulphur.

E. G.

A Quick-acting Potash Apparatus. GUSTAV SCHÖLER (*Chem. Zeit.*, 1905, 29, 569—570).—The pear-shaped inner vessel, *I*, is partly filled

with a solution prepared by dissolving 5 grams of curd soap in 150 c.c. of hot water and 50 grams of potassium hydroxide. The carbon dioxide generated in the combustion is very rapidly absorbed, and may be passed at a much more rapid rate than usual, as the absorption is accelerated by the lather formed. The unabsorbed gases now pass into the outer vessel, *II*, containing a little of a solution of 100 grams of potassium hydroxide in 100 c.c. of very hard water, to which, if necessary, a little calcium chloride may be added. They finally escape through the calcium chloride tube.



L. DE K.

Assay of Salpetre. R. BENSEMANN (*Zeit. angew. Chem.*, 1905, 18, 816).—A weighed portion of the sample is dissolved in water, mixed with at least twice its weight of oxalic acid, and evaporated to dryness on the water-bath. The dry mass is then moistened with water and again evaporated, and this operation is repeated several times.

In this way, the nitrate is completely converted into oxalate; any chlorides are similarly decomposed, but perchlorates and sulphates are not affected. If now the mixture is gradually heated to redness, the mass will contain potassium (or sodium) carbonate derived from the nitrate and any chloride, and also potassium chloride due to the perchlorate.

The alkali carbonate is now estimated in an aliquot part of the solution by titration with standard acid and, after allowing for the chloride, estimated in another portion of the sample, the nitrate is calculated. The chlorine which is estimated in another portion of the solution represents the perchlorate. A third portion may be used for estimating any sulphate.

L. DE K.

Rapid Estimation of Calcium, Potassium, and Phosphoric Acid. ERNST H. SCHULTZE (*Chem. Zeit.*, 1905, 29, 508—509).—*Estimation of Calcium in Limestones, Mortars, &c.*—The substance is dissolved in dilute hydrochloric acid with addition of a little nitric acid. After boiling with a slight excess of ammonia, the cold liquid is diluted to a definite volume, and an aliquot part, after acidifying with acetic acid, is precipitated with a known weight of ammonium oxalate. The excess of oxalate is then determined in an aliquot part of the filtrate. In the presence of decided quantities of phosphoric acid, the ammoniacal precipitate is redissolved by means of hydrochloric acid, and, after adding a little ferric chloride, the phosphoric acid and the excess of iron are precipitated by boiling with sodium acetate. After again boiling with a little ammonia, the filtrate is treated as already directed.

Estimation of Potassium in Kainites, &c.—The sample is boiled with dilute hydrochloric acid (1:25) and carefully precipitated with barium chloride. An aliquot part of the filtrate (=about 0.4 gram of the sample) is then treated with 0.5 c.c. of platinic chloride (1:10) and then gradually with 120 c.c. of hot 96 per cent. alcohol. Mechanical stirring is resorted to for about 20 minutes, when the precipitate is collected on a Gooch filter, washed with alcohol, finally with ether, and dried at 120°.

Volumetric Estimation of Phosphoric Acid.—Pemberton's process is recommended. The aqueous or sulphuric acid solution of the phosphate is neutralised with potassium hydroxide, acidified with nitric acid, mixed with ammonium nitrate, and heated to 80°. The phosphoric acid is then precipitated with ammonium molybdate, and the yellow precipitate is collected and washed first with 1 per cent. nitric acid, and then twice with cold water. The precipitate is then dissolved in a known volume of standard potassium hydroxide, the excess of which is titrated with standard hydrochloric acid, using phenolphthalein as indicator.

L. DE K.

Solubility of Lime and Magnesia in Solutions of Sodium Chloride with or without Sodium Hydroxide. Application to the Separation and Estimation of the Two Substances. E. MAIGRET (*Bull. Soc. chim.*, 1905, [iii], 33, 631—634).—The author finds that whilst lime is fairly soluble, magnesia is insoluble in solutions containing up to 160 grams per litre of sodium chloride in presence of 0.8 gram per litre of sodium hydroxide. This difference has been utilised in extending and rendering more accurate D'Anselme's method of estimating lime and magnesia (*Abstr.*, 1903, ii, 695). One hundred c.c. of the liquid are placed in a 200 c.c. flask, and 20 c.c. of a solution containing sodium carbonate (100 grams per litre) and sodium

hydroxide (20 grams per litre), the equivalent of which in 2*N*-hydrochloric acid is known, are added. The mixture is heated to boiling, then cooled and made up to 200 c.c. with a solution of sodium chloride (160 grams per litre). The mixture is shaken and filtered and 100 c.c. of the filtrate titrated with 2*N*-hydrochloric acid using tropeolin as indicator. The difference between twice the burette reading and the equivalent of the alkaline solution added is equal to the total magnesia and lime present in terms of 2*N*-hydrochloric acid.

For the estimation of the magnesia alone, 100 c.c. of the solution are mixed with 10 c.c. of a solution of sodium hydroxide (80 grams per litre), diluted to a litre with a solution of sodium chloride (160 grams per litre), and, after shaking, filtered and 500 c.c. of the filtrate titrated with 2*N*-hydrochloric acid, using phenolphthalein as indicator. The difference between the burette reading multiplied by 2 and the titre of the sodium hydroxide solution added is equivalent to the magnesia present. The difference between this and the first estimation gives the equivalent of the lime present. T. A. H.

Estimation of Lead by Persulphate in Acid Solution. MAX DITTRICH and A. REISE (*Ber.*, 1905, 38, 1829—1831).—When ammonium persulphate solution is added to a solution of a lead salt, the lead is quantitatively precipitated as white crystals, which darken when the liquid is heated at 80° for 3 hours in presence of a little silver nitrate, the precipitate then consisting of a mixture of lead oxide and peroxide together with a small quantity of lead sulphate. The precipitate is washed with a 3 per cent. solution of ammonium sulphate and is converted into lead sulphate by igniting with a drop of sulphuric acid. The best precipitant consists of a 2 per cent. ammonium persulphate solution containing a trace of silver nitrate; this should be heated to 80° and the lead solution added to it drop by drop. T. H. P.

Estimation of Copper and Free Matte in Dross. VALLETY (*Ann. Chim. anal.*, 1905, 10, 193).—Five grams of the dross are treated with 100 c.c. of a 5 per cent. solution of silver nitrate and 5 c.c. of nitric acid are added. After 24 hours, the solution is filtered and the copper estimated by the usual process. L. DE K.

Mass Analyses of Muntz Metal by Electrolysis. Electrolytic Properties of the Alloy. JOHN G. A. RHODIN (*Trans. Faraday Soc.*, 1905, 1, 119—135).—The paper contains the results of experiments to find a method for the accurate estimation of the copper in Muntz metal of sufficient rapidity to give about 100 determinations daily within 12 hours of the time of casting. The method adopted was an electrolytic method, for which the author claims an accuracy of 0.07 per cent. and the necessary speed and ease of working. The experimental details are given. For Muntz metal to be a successful ship sheathing it is necessary that it should dissolve electrolytically in sea-water to a sufficient extent to render the surface poisonous, but sufficiently slowly to make its use economical, and the best result will

be obtained when the two components of the alloy dissolve at equal rates. Assuming the rate of dissolution to be directly proportional to the heat of formation of the ultimate compounds and to the electrical conductivity of the dissolving metal, the author obtains theoretically the proportion 60.8 Cu, 30.2 Zn as that of the best alloy, a result in accord with practical experience. The results of experiments on the rate of dissolution are appended, and it is seen that barometric pressure has a considerable effect on the velocity of dissolution. L. M. J.

Titrimetric Method of Estimating Mercury. ERWIN RUPP (*Arch. Pharm.*, 1905, 243, 300—302).—A few c.c. of formaldehyde solution (about 35 per cent.) are made alkaline with dilute aqueous alkali hydroxide, a suitable quantity of the mercury solution is added, and the mixture is shaken and warmed for 10—15 minutes on the water-bath. The liquid is then acidified with plenty of acetic acid, a suitable volume of $N/10$ iodine solution is added, the flask is corked and shaken gently for 5 minutes or so (until the precipitate of metallic mercury has all gone into solution as potassium mercuriodide), and the excess of iodine is titrated with $N/10$ thiosulphate in the presence of starch solution. Each 1 c.c. of the $N/10$ iodine solution used = 0.01002 gram of mercury or 0.01355 of mercuric chloride. The method is applicable in the presence of chlorides, unlike the titration with thiocyanate solution. C. F. B.

Standardisation of Potassium Permanganate Solutions by means of Silver. KARL HOPFGARTNER (*Monatsh.*, 1905, 26, 469—482).—A weighed amount of silver is dissolved in a solution of ferric ammonium sulphate acidified with sulphuric acid, and the ferrous salt so formed titrated with the potassium permanganate solution to be standardised. G. Y.

Estimation of Ferric Oxide in presence of much Alumina. ERNST DEUSSEN (*Zeit. angew. Chem.*, 1905, 18, 815—816).—The usual plan is to fuse the strongly ignited and weighed mixed oxides with potassium pyrosulphate. The mass is then dissolved, the iron is reduced to the ferrous state and titrated with permanganate. In order to save time and prevent damage to the platinum crucibles, which are attacked by potassium pyrosulphate, the author prefers fusing with about 1 gram of potassium hydrogen fluoride instead. After fusing for a few minutes over a small Bunsen flame, the mass turns solid. The bulk of the hydrogen fluoride is now expelled by heating with dilute sulphuric acid, and the resulting solution is treated as usual. L. DE K.

Electrolytic Estimation of Molybdenum. ALBERTO CHILESOTTI and A. ROZZI (*Gazzetta*, 1905, 35, i, 228—236).—For the electrolytic estimation of molybdenum in solutions of molybdates (compare Kollock and Smith, *Abstr.*, 1901, ii, 694), the concentration of the sulphuric acid in the solution should not be less than $N/100$ nor more than $N/10$, the percentage of molybdenum trioxide in the form of ammonium molybdate being about 0.1. The presence of salts of the

alkali metals, such as potassium sulphate or nitrate or sodium sulphate, leads in some cases to high results, the alkali being to some extent precipitated with the molybdenum. In presence of small quantities of salts of the alkali metals (less than 0.75 per cent. of K_2SO_4), this inaccuracy may be avoided by acidifying the solution with 0.4—0.5 per cent. of sulphuric acid. With larger quantities of salts of alkali metals, it is necessary to convert the precipitated molybdenum trioxide into ammonium molybdate, acidify the solution of the latter with 0.4—0.5 per cent. of sulphuric acid, and reprecipitate the molybdenum electrolytically. When the alkali metals have also to be estimated, this must be done in the combined residual liquors from the two electrolyses. The precipitate of molybdenum trioxide is more easily dealt with when it is deposited in a matt platinum vessel.

T. H. P.

Estimation of Gold and Platinum by means of Magnesium.

FRANZ FAKTOR (*Chem. Centr.*, 1905, i, 1305—1306; from *Pharm. Post*, 38, 175. Compare this vol., ii, 455).—When a solution of gold chloride is boiled with magnesium ribbon until the solution is colourless and a fresh piece of ribbon is no longer tarnished, the gold separates completely in the form of brownish-yellow flakes, and may be weighed in a pure form after dissolving the excess of magnesium in hydrochloric acid. In the case of gold alloys, the excess of acid must be removed before adding the magnesium, and the metals which are precipitated with the gold must be removed by the action of a suitable acid. The same method may be used for the separation of platinum from the brownish-yellow solution of the chloride.

E. W. W.

Reaction of Rhodium. EUGENIO P. ALVAREZ (*Compt. rend.*, 1905, 140, 1341—1343; *Chem. News*, 1905, 91, 216).—Excess of sodium hydroxide is added to an aqueous solution of a rhodium salt to produce an alkaline solution of rhodium sesquihydroxide, $Rh(OH)_3 \cdot H_2O$. Into this is passed the gas evolved by the action of hydrochloric acid on potassium chlorate. The liquid becomes yellowish-red, then red, and finally a slight green precipitate forms and redissolves in the liquid yielding a blue solution (Claus' blue), due to the production of sodium perrhodate, Na_2RhO_4 . The colour is insoluble in ether or benzene, and is destroyed by sulphur dioxide, sodium peroxide, or sodium persulphate.

T. A. H.

Mineralogical Analysis of Soils. J. DUMONT (*Compt. rend.*, 1905, 140, 1111—1113).—Soils which contain much vegetable matter are trituated in a 60 per cent. solution of calcium nitrate which has a sp. gr. greater than that of humus. The soil is then boiled with oxalic acid in such quantity that 10 per cent. (of the weight of the soil) remains after all the calcium carbonate is decomposed. (Or the calcium carbonate may be decomposed by mineral acids before treatment with oxalic acid.) The heating in a salt-bath is continued for an hour. It is then filtered, washed first with water containing nitric acid to remove the calcium oxalate, and then with distilled water, after which it is digested for a day or two with an ammoniacal

solution which dissolves the humus. Sand and silicates are removed centrifugally, the clay remaining in suspension whilst the sand settles. Half an hour, at the rate of 1000 rotations, generally suffices. The liquid is poured off, fresh ammoniacal water added, and the process repeated. This is continued until a clear liquid remains. The sand is then collected and may be separated into fractions of different degrees of fineness by sieves.

Different mineral constituents—mica, felspar, and quartz, &c.—are separated by means of liquids of different densities (mercuric iodide dissolved in potassium iodide, methylene iodide with varying amounts of xylene, &c.) in conjunction with centrifugalising.

N. H. J. M.

A Filter Funnel for the Estimation of Paraffin in Mineral Oil Distillates. JULIUS FLEISCHER (*Chem. Zeit.*, 1905, 29, 489).—The apparatus consists of a cylindrical porcelain funnel, destined to contain a Soxhlet extraction capsule, which is surrounded by a larger funnel containing a freezing mixture at -18° to -20° , thus enabling the liquid to be filtered at a low temperature. It is claimed for the apparatus, which is in one piece, that by its use 8 to 10 estimations can be performed in the time usually required for one.

P. H.

Refractometric Analysis of Beer. EDWIN ACKERMANN (*Ann. Chim. anal.*, 1905, 10, 171—178).—The beer is well shaken to deprive it of its carbon dioxide and is passed through a filter. The sp. gr. is then very carefully taken at 15° and also its refraction at 17.5° , using a Zeiss immersion refractometer.

By means of a disc-shaped calculating machine, fully described and illustrated in the original article, both the percentage of alcohol and extract may be readily ascertained.

L. DE K.

Some Conditions affecting the Ester Value of Brandy. PHILIP SCHIDROWITZ and FREDERICK KAYE (*Analyst*, 1905, 30, 149—152).—The authors found that ordinary tap-water, such as the New River supply, when used for "breaking down" brandy, caused a decrease of 15 per cent. or more in the ester value other than that due to the dilution. This water also appreciably affected the acid value of the brandy. An examination of new brandy bottles showed that in some cases the bottles yielded a distinct quantity of alkali to distilled water. The total acid in a blended brandy was found to be by no means necessarily equivalent to the theoretical mean of the constituents. Blending also affected the ester value, the deviations from the mean being, in a few instances, quite appreciable.

W. P. S.

Estimation of Higher Alcohols in Spirits. I. PHILIP SCHIDROWITZ and FREDERICK KAYE (*Analyst*, 1905, 30, 190—197).—The Beckmann process (*Abstr.*, 1902, ii, 178) was found to give untrustworthy results, the fault lying in the actual extraction and not in the nitration part of the process. In the Allen-Marquardt method, a certain quantity of ethyl alcohol remained in the carbon tetrachloride extract, but for some unexplained reason disappeared during the oxidation with the

chromic acid mixture. It was not converted into acetic acid, and the authors suggest that it was either oxidised into carbon dioxide and water or formed a neutral ester with the mineral acid present.

W. P. S.

Colour Reactions of Pyruvic Acid with α - and β -Naphthols in Sulphuric Acid Solution. EUGENIO P. ALVAREZ (*Chem. News*, 1905, 91, 209).—When pyruvic acid is added to β -naphthol dissolved in strong sulphuric acid, a red coloration is produced, which, when gently warmed, becomes deep blue; on addition of water or alcohol a fugitive yellow colour is obtained. With α -naphthol under similar conditions, the first solution is yellow, changing to a deep orange varnish when warmed and spread over the capsule employed; the colour is not changed by water.

D. A. L.

Volumetric Estimation of Reducing Sugars. ARTHUR R. LING and THEODORE RENDLE (*Analyst*, 1905, 30, 182—190).—To ascertain the exact end-point when a sugar solution is titrated with Fehling's solution, the use of ferrous thiocyanate as an indicator is recommended. This is prepared by dissolving 1 gram each of ferrous ammonium sulphate and ammonium thiocyanate in 10 c.c. of water at a temperature of 45—50°, cooling immediately, and adding 50 c.c. of concentrated hydrochloric acid. If the solution has a reddish-brown colour, due to the presence of ferric salt, the latter is reduced by the addition of a little zinc-dust. When a drop of the titration liquid is brought into contact with a drop of the indicator, a red coloration is produced as long as cupric salt is present. Examples are given of estimations of invert sugar, dextrose, maltose, molasses, &c., showing that the method is capable of a high degree of accuracy. W. P. S.

Use of the Orcinol Reaction for the Detection of Sugar in Urine. GUIDO MANN (*Chem. Centr.*, 1905, i, 1438; from *Berl. klin. Woch.*, 42, 231—232).—Neumann (*Berl. klin. Woch.*, 41, No. 41) has used a modification of the orcinol reaction to distinguish between the hexoses. This may be used with great advantage in the investigation of urine. In slight cases of diabetes, the dextrose colour test with orcinol is successful where other tests fail; 0.1 per cent. can be detected easily. The reaction for lævulose is sharp, and the detection of lævulosuria easy. Albumin, if present in the urine, should be removed before applying the test.

W. D. H.

Estimation of Maltose or Dextrose in presence of Starch Paste. JULES WOLFF (*Ann. Chim. anal.*, 1905, 1, 193—195).—The estimation of maltose in the presence of non-liquefied starch presents some physical difficulties. The author has succeeded in overcoming these by liquefying this starch by heating for 7 or 8 minutes at 72° with a small quantity of infusion of malt. As this, however, produces an additional amount of maltose, a check experiment must be carefully made, using the same amount of malt for the same volume of starch solution of approximately the same strength, and heating for exactly the same time at the same temperature. The further

action of the malt is stopped by plunging the flasks for a few minutes into boiling water.

L. DE K.

Apparatus for Heating Substances in a Vacuum at Constant Temperatures. WILLIAM R. HODGKINSON and ARTHUR H. COOTE (*Chem. News*, 1905, 91, 194).—An apparatus suitable for carrying out the "stability test" for gun-cotton and similar purposes is described and figured. The substance is held in a tube which is suspended in a heating vessel, and is suitably connected with an exhaust pump, and, if required, with a measuring tube in which the gases evolved may be collected.

D. A. L.

Methods for Estimating Formaldehyde. R. H. WILLIAMS (*J. Amer. Chem. Soc.*, 1905, 27, 596—601).—After having tried the standard methods, the author arrives at the following conclusions. Romijn's iodometric method (Abstr., 1897, ii, 166) is very accurate for pure dilute solutions of formaldehyde, whilst Romijn's cyanide process (*ibid.*, 167) may be recommended for dilute impure solutions; the results are lower than those obtained by the oxidation methods. Blank and Finkenbeiner's method (Abstr., 1899, ii, 188, 820), based on oxidising the formaldehyde with hydrogen peroxide in an alkaline solution and titrating the excess of alkali with litmus as indicator, is the most satisfactory for strong impure solutions. Legler's ammonia process (Abstr., 1883, 1035) is not so satisfactory, as the end-point in the titration is not defined very sharply. Paraformaldehyde, when present, counts as formaldehyde.

L. DE K.

Colorimetric Method for the Detection and Estimation of Formaldehyde. FREDERIC BONNET, jun. (*J. Amer. Chem. Soc.*, 1905, 27, 601—605).—Sixty c.c. of the liquid (milk, for instance) are placed in a 3-inch evaporating dish, and a 1-inch watch-glass containing 1 c.c. of morphine solution is allowed to float on it. The whole is then immediately covered with a 4 × 5-inch glass plate, and heated, preferably, at 25°.

The morphine solution is prepared by dissolving, just before use, 0.35 gram of pure morphine sulphate in 100 c.c. of chemically pure sulphuric acid. If formaldehyde should be present in the milk, the morphine becomes more or less coloured, and a ring is formed varying from pink to blue. By operating under exactly similar conditions with milks to which a known amount of formaldehyde has been added, and by noticing particularly the time required for the formation of the ring, a fair idea may be obtained as to the amount of formalin in any given sample. As a qualitative process, the method is also applicable to solid foods, such as butter.

L. DE K.

Detection of Formaldehyde in Milk. E. NICOLAS (*Compt. rend.*, 1905, 140, 1123—1124).—The author employs a modification of Manget and Marion's reaction (Abstr., 1903, ii, 115). The milk to be tested is curdled by the addition of a little acetic or lactic acid. After filtration, a quantity (an excess) of "amidol" is added to the filtrate, when, in a short time, the solution is coloured yellow or

orange and becomes strongly fluorescent should formaldehyde be present. In the absence of formaldehyde, the coloration rapidly becomes red, then brown, but without fluorescence. The test will detect 1 part of formaldehyde in 500,000.

W. P. S.

The Vanillin-hydrochloric Acid Reaction. LEOPOLD ROSENTHALER (*Zeit. anal. Chem.*, 1905, **44**, 292—301).—Various ketones, such as acetone, diethyl ketone, dipropyl ketone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, pinacoline, acetylacetone, acetonylacetone, benzylideneacetone, levulose, and in general all aliphatic ketones yield characteristic colour reactions with the vanillin-hydrochloric acid reagent. It is merely necessary to expose filter paper wetted with the reagent to the vapour of the ketone. On the other hand, phenyl ethyl ketone, benzoylacetone, acetophenone, benzylideneacetophenone, benzophenone, tetramethyldiaminobenzophenone, benzoin, benzil, anthraquinone, and most of the aromatic ketones give a negative result. The reaction is in some cases extremely sensitive. If the reagent is mixed with an equal volume of concentrated sulphuric acid, one or two drops of a 0.01 per cent. solution of acetone will produce a violet colour on warming. Similar reactions are obtained with a large number of essential oils and some balsams, but with these it is necessary to shake the cooled mixture with ether to remove from the aqueous solution other colouring matters which would obscure the reaction. In some cases small amounts of adulterants can be detected by this means.

M. J. S.

Phenolphthalin as Reagent for Hydrogen Cyanide. F. WEEHUIZEN (*Chem. Centr.*, 1905, i, 1191; from *Pharm. Weekbl.*, **42**, 271—272).—On addition of a solution of phenolphthalin rendered alkaline with sodium hydroxide and about 1/2000 of a copper sulphate solution to a solution containing hydrogen cyanide, the phenolphthalin is oxidised in the cold to phenolphthalein and the liquid turns red. One part of hydrogen cyanide in 500,000 parts of a liquid still gives the reaction.

L. DE K.

Estimation of Cyanogen Iodide in presence of Iodine. JAR. MILBAUER and R. HAC (*Zeit. anal. Chem.*, 1905, **44**, 286—292).—It has been frequently stated that commercial iodine is liable to contain cyanogen iodide, but the methods of estimating that impurity have been very unsatisfactory. It can, however, be effected by Kjeldahl's process. The substance is triturated with concentrated sulphuric acid and transferred to the Kjeldahl flask with an equal volume of water. The mixture is cautiously heated to expel the free iodine with the aqueous vapour, and when this is complete the temperature is raised and the operation completed in the usual manner. Test experiments gave good results, but the impurity was not found in any of the specimens of commercial iodine examined.

M. J. S.

Estimation of Oxalic Acid by Permanganate in presence of Hydrochloric Acid. GREGORY P. BAXTER and JOAQUIN E. ZANETTI (*Amer. Chem. J.*, 1905, 33, [v], 500—506).—It is a well-known fact that a hydrochloric acid solution of an oxalate cannot be accurately titrated with permanganate unless a certain quantity of manganous sulphate is added. According to the author's investigation, this is due to the formation of hypochlorous acid. This may, however, be prevented by operating under well-defined conditions, when the results will be quite trustworthy.

The oxalic acid, which should amount to about 0.3 gram, is dissolved in 20 c.c. of hydrochloric acid of sp. gr. 1.04, diluted with water to 150 c.c. After heating to a little above 70°, a standardised solution of potassium permanganate (4 grams per litre) is run in very slowly and with constant stirring until the liquid turns pink. No oxalic acid is decomposed or volatilised, even at 90°. L. DE K.

Improved Apparatus for Use in the Gottlieb-Röse Method of Estimating Fat in Milk. ARMIN RÖHRIG (*Zeit. Nahr. Genussm.*, 1905, 9, 531—538).—To avoid pipetting off a portion of the ethereal layer obtained in this method, the milk is treated with ammonia, alcohol, ether, and light petroleum as usual in a stoppered, graduated cylinder provided with a side-tube and tap at about the 25 c.c. mark on the graduations. By means of this tap, an aliquot part of the ethereal solution may be drawn off into a weighed flask. The percentage of fat in butter may also be estimated by this method and apparatus. W. P. S.

Rapid Method for the Analysis of Milk. FRED. BORDAS and TOUPLAIN (*Compt. rend.*, 1905, 140, 1099—1100).—Ten c.c. of the milk are added drop by drop to a mixture of 65 per cent. alcohol and acetic acid contained in a weighed tube. After a few minutes, the tube and its contents are subjected to centrifugal action and the clear solution decanted. The residue is washed with 30 c.c. of 50 per cent. alcohol, separated, and decanted. The lactose in the united alcoholic solutions is then estimated according to Fehling's method. To dissolve the butter-fat from the residue remaining in the tube, the latter is twice treated with 2 c.c. of 96 per cent. alcohol and 30 c.c. of ether. Separation is effected each time in the centrifugal machine, and the ethereal solutions are evaporated in a tared flask. The casein remaining in the tube is then dried and weighed. An estimation of the ash on a separate 10 c.c. of the milk completes the analysis. In applying the method to sour milk, the total volume of the latter is noted, and the sample then separated by centrifugal action into two layers which are analysed separately. W. P. S.

[Occurrence of Ammonia in Contaminated Milk.] AUGUSTE TRILLAT and SAUTON (*Compt. rend.*, 1905, 140, 1266—1268).—It is shown that milk inoculated with urine or other animal matter almost always contains appreciable quantities of ammonia. The authors consider that, whilst the absence of ammonia is not a positive proof of the purity of the milk, its presence affords an assumption that the milk is contaminated with animal excreta. The method of detecting ammonia

in milk is a modification of the one previously described by Trillat (Abstr., 1905, ii, 282). Ten c.c. of the milk are treated with 10 c.c. of a 10 per cent. solution of iodine trichloride. The precipitate, consisting of the proteids and fat, is collected on a filter. To the filtrate is added, little by little, milk of lime until a dense black coloration, due to the formation of nitrogen iodide, is obtained.

W. P. S.

Cachalot Oil. GEORG FENDLER (*Chem. Zeit.*, 1905, 29, 555—556).—The author describes the examination of a sample of cachalot oil. It deposited crystals of spermaceti melting at 42°. Glycerol was detected in the oil, and an examination of the fatty acids was made.

A. McK.

Influence of Atmospheric Oxidation on the Constants of Oils. II. HENRY C. SHERMAN and M. J. FALK (*J. Amer. Chem. Soc.*, 1905, 27, 603—608. Compare Abstr., 1903, ii, 703).—The authors state that an oil with a low iodine number and specific refractive power, high sp. gr., index of refraction, and Maumené number may be considered to be partly oxidised by exposure or “blowing.”

The original iodine number of a partly oxidised oil may be obtained with a fair degree of accuracy by adding to the iodine number found 0.8 for every 0.001 increase in the sp. gr. $15.5^{\circ}/15.5^{\circ}$. This correction, however, only applies to non-drying and semi-drying oils.

If the original sp. gr. of the sample cannot be obtained, the calculation may be based on the average sp. gr. of the species under examination.

L. DE K.

Stovaine. F. ZERNIK (*Chem. Centr.*, 1905, i, 1028; from *Apoth. Zeit.*, 20, 174—175).—Stovaine, the hydrochloride of α -dimethylamino-*tert*-amyl benzoate, $\text{OBz} \cdot \text{CMeEt} \cdot \text{CH}_2 \cdot \text{NMe}_2 \cdot \text{HCl}$ (Fourneau, Abstr., 1904, i, 377), gives precipitates with the ordinary alkaloidal reagents in a 1 per cent. solution. The following test is characteristic. When 0.05 gram of stovaine is evaporated with 1 c.c. of a mixture of equal parts of hydrochloric acid and nitric acid on the water-bath, a colourless compound which has a pungent odour is obtained. If 1 c.c. of a solution of potassium hydroxide in alcohol is added and the mixture evaporated, the residue has a fruity odour, and oily drops separate on addition of water. Stovaine may be used as a substitute for cocaine (compare Abstr., 1904, ii, 501).

E. W. W.

New Reagent for Aconitine. EUGENIO P. ALVAREZ (*Chem. News*, 1905, 91, 179—180).—When a minute quantity of aconitine is slightly heated with bromine in a porcelain crucible, evaporated to dryness with nitric acid, again treated with bromine, and evaporated to dryness with alcoholic potash, a red or brown residue is obtained, which becomes a deep green when treated with a 10 per cent. solution of copper sulphate.

D. A. L.

Assay of Opium and its Preparations. WALTER HENRY LENTON (*Pharm. J.*, 1905, 74, 652—653).—In the method described, the British Pharmacopœia process is followed up to the filtration of the

alkaline solution. Fifty c.c. of the latter are placed in a separating funnel, a plug of cotton-wool covered with a thin layer of disintegrated filter-paper or asbestos having been previously placed in the constriction above the tap. The requisite quantities of ether, alcohol, and ammonium chloride are added, the mixture is thoroughly shaken, care being taken not to dislodge the plug, and set aside for the specified time. The liquid is then forced through the plug by air-pressure applied by means of an ordinary bellows, and the residue washed twice with 20 c.c. of a mixture of equal volumes of ether and morphinated water. Finally, the contents of the funnel are washed with morphinated water until free from chlorides, and then quickly with 2 c.c. of water. Twenty-five c.c. of *N*/10 acid are now added to the funnel, the latter is shaken violently to dislodge the plug, and the excess of acid titrated back with *N*/20 sodium hydroxide, using methyl-orange as indicator.

W. P. S.

Analysis of Tanning Materials. JOHANNES PAESSLER (*Zeit. anal. Chem.*, 1905, 44, 301—304).—The author is not prepared to accept the opinion of Wislicenus (compare this vol., ii, 363) that exfoliated alumina should be substituted for hide-powder in the estimation of tannin. Its behaviour under varied conditions must first be thoroughly investigated and a consensus of opinion obtained with regard to the mode of preparing it and the uniformity of the results which it yields.

M. J. S.

Mustard Seed. C. HARTWICH and A. VIULLEMIN (*Chem. Centr.*, 1905, i, 1032—1033; from *Apoth. Zeit.*, 20, 162—164).—Myrosin is best detected by heating filtered aqueous extracts with a few drops of freshly prepared Millon's reagent. In the case of seeds of *Brassica nigra*, a reddish-brown precipitate is obtained, whilst with *Sinapis alba* the solution itself acquires an intense red colour. *Sinapis dissecta* and *S. arvensis* behave similarly to *S. alba*, so that an addition of *S. alba* and *S. arvensis* to black mustard is easily detected. In detecting myrosin microscopically in mustard seeds, the sections are washed with ether and chloroform, and treated successively with dilute acetic acid and cold concentrated hydrochloric acid (which produces a violet coloration) or with Millon's reagent. The ethereal oil is determined by Dieterich's method. The finely powdered seed (5 grams) is frequently agitated with water (100 c.c.) at 25—30°. Alcohol (20 c.c.) is then added and about half distilled off into ammonia (30 c.c.) and alcohol (20 c.c.), the first receiver being connected with a second, also containing ammonia and alcohol, to prevent loss. The contents of the receivers are united and heated on a water-bath with 3—4 c.c. of 10 per cent. silver nitrate and filtered. The silver sulphide is dried at 80° and weighed. The result, multiplied by 8.602, gives the percentage amount of ethereal oil. Seeds of *Brassica nigra* were found to contain from 0.825 to 1.191 per cent.

N. H. J. M.

General and Physical Chemistry.

Relation of Electrolytic Dissociation to Refractive Power: Non-electrolytes in Solution. IVO ZOPPELLARI (*Gazzetta*, 1905, 35, i, 355—368).—Refractometric measurements of solutions of naphthalene, thymol, camphor, carbamide, and sucrose in benzene, methyl alcohol, acetone, and water show that the refractive powers vary with the concentrations of the solutions, the variations being of the same order as those shown by solutions of electrolytes. These variations depend either on a specific action of the solvent, which is, however, different for different substances, and may be related to the changes of volume occurring during solution, or on the inexactitude of the formulæ used to express refractive power, or on the fact that the law of mixtures is not rigorously applicable in all cases. Since the variations here observed are similar to those exhibited by electrolytes, the conclusions drawn with regard to the latter from the theory of electrolytic dissociation must be regarded as insecure. T. H. P.

Photographs of Spark Spectra. III. Ultraviolet Spark Spectra of Platinum and Chromium. WALTER E. ADENEY (*Sci. Proc. Roy. Dubl. Soc.*, 1904, 10, 235—249. Compare Abstr., 1902, ii, 57).—A full list is given of the wave-lengths of the lines observed. J. C. P.

Absorption Spectra of Solutions of Chrome Alum. EFISIO FERRERO and M. NOZARI (*Atti R. Accad. Sci. Torino*, 1904—1905, 40, 453—462. Compare Abstr., 1901, ii, 203).—The absorption spectrum of a solution of chrome alum exhibits increasing absorption from the red to the yellow, where it has a maximum value; the absorption then diminishes to the green, after which it increases again and becomes very great in the violet portion of the spectrum.

Like the internal friction (*loc. cit.*), the absorption spectrum of solutions of chrome alum shows a distinct change when the temperature is raised until the blue colour changes to green. The absorption spectrum of the blue solution presents a black band, the least deviated edge of which gradually fades away, whilst the end which is most deviated is sharp; the former edge approaches the red when the solution becomes green. The absorption curves for different temperatures show that the slope of the diminution of the absorption, which takes place as far as $\lambda = 580$, is very slight for temperatures below 67° , but at the latter temperature the slope becomes very distinct and remains the same at all higher temperatures. The maximum absorption for temperatures below 67° occurs at $\lambda =$ about 489, whilst at or above 67° the maximum is at $\lambda =$ about 497.

Curves and tables of the results are given.

T. H. P.

Rotation of Optically Active Substances. CHR. WINTHER (*Zeit. physikal. Chem.*, 1905, 52, 200—208. Compare Abstr., 1902, ii, 589; 1904, ii, 4).—A discussion, suggested by Walden's recent lecture

(this vol., ii, 130), of the most advantageous lines of future research on optical activity. The author insists on the necessity of determining rotation at different temperatures, and for light of different wavelengths, otherwise characteristic maxima remain undetected. As a measure of the rotation dispersion, the author advocates the use of dispersion coefficients in preference to that of specific and molecular rotation dispersion, and urges that whilst the five Landolt colours should be taken into account, yellow should be chosen as the standard to which the others are referred. The author argues against the form of temperature coefficient suggested by Walden, and considers that the variation of rotation with temperature should be represented by an equation of the type $[\alpha]_t = a \pm bt \pm ct^2$. Further, the bearing of time, variety of light, and temperature on the behaviour of each solvent should be investigated in detail. The value of this sort of work is seen to a certain extent in the "solution dispersion coefficients" previously determined (Winther, *loc. cit.*). J. C. P.

Limits of Visibility of Fluorescence and the Higher Limit of the Absolute Weight of Atoms. WALTHER SPRING (*Rec. Trav. chim.*, 1905, 24, 297—304. Compare de Bruyn and Wolff, *Abstr.*, 1904, ii, 470).—The fluorescence of a solution of fluorescein or of eosin in optically transparent water (*Abstr.*, 1899, ii, 537) becomes invisible in daylight when the amount of the fluorescent substance present falls to 0.000,000,01 gram per c.c., and is just visible at the apex of a powerful beam of electric light when the concentration is 0.000,000,000,000,001 gram per c.c. It is found that the area of liquid illuminated by the apex of the cone of light must be at least 1 sq. mm. in order to render the fluorescence visible, and consequently, assuming that 1 cubic millimetre of the liquid contains at least one molecule of fluorescein (mol. wt. 408) for example, then the weight of an atom of hydrogen would be 2.5×10^{-21} grams. This value, which represents only the higher limit among possible values, is much smaller than those arrived at from other considerations by Clerk Maxwell, Kelvin, de Heen, Annaheim, and others. T. A. H.

Crystalloluminescence and Triboluminescence. MAX TRAUTZ and P. SCHORIGIN (*Zeit. Elektrochem.*, 1905, 11, 306—307).—Many substances exhibit temporary triboluminescence consisting in bluish-white sparks produced in the crystals when they are broken. Among these are crystals of arsenic trioxide (from acid solution) and of sodium bromate. The following substances show feeble permanent triboluminescence in addition to the temporary phenomenon (which disappears in some days or weeks after the crystals are made): Barium chlorate, barium, strontium, calcium and magnesium bromates, potassium sodium sulphate ($2K_2SO_4, Na_2SO_4$), and potassium sulphate crystallised from a solution containing potassium hydrogen sulphate and sodium fluoride.

Crystalloluminescence was observed with all substances possessing triboluminescence; it is probably the same phenomenon caused by impacts of the crystals on each other as they are formed in the solution. T. E.

Sensitiveness of Photographic Action due to Hydrogen Peroxide. J. PRECHT and C. OTSUKI (*Zeit. physikal. Chem.*, 1905, 52, 236—238. Compare this vol., ii, 296).—By means of its action on a photographic plate it is possible to detect hydrogen peroxide in the concentration 3×10^{-9} grams per c.c. of space. J. C. P.

Some Properties of the α -Rays from Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1905, [vi], 10, 163—176).—The paper contains preliminary results of an attempt to determine the velocity and the ratio e/m of the α -particle emitted from radium. It has been shown by Bragg and Kleeman (this vol., ii, 5) that four sets of α -rays are emitted from radium, each capable of producing ionisation through a definite and different distance in air (that is, probably, each set is of a definite velocity), and that the ionisation power ceases abruptly at the limiting distance. The source of the α -rays employed by the author was the deposit on the thin wire which had been negatively charged in the presence of radium bromide, and under the conditions of the experiment the rays examined would be almost entirely those from radium C. The deflection of the path by a strong magnetic field showed no widening of the cone of rays, so that all the particles were travelling with the same velocity. The value of mV/e obtained from the deflection was 3.98×10^5 . The deflection by an electric field has not been determined, but on the assumption that the heating effect of radium C is entirely due to the α -particles, the value for mV^2/e is obtained at 1.03×10^{16} . These lead to $V = 2.6 \times 10^9$ cms. per second, and $e/m = 6.5 \times 10^3$ electromagnetic units; a result in good accord with previous estimates. The effect of sheets of thin aluminium foil on the velocity was also investigated, and it was found that although a clear photographic impression was obtained after passage through 12 sheets (0.00031 cm. each), no effect was obtained after passage through 13 sheets, and the relative velocities after passing through various thicknesses are given, thus: $V_0 = 1.00$; 5 sheets, $0.85V_0$; 10 sheets, $0.73V_0$; 12 sheets, $0.64V_0$. The energy after passage through 12 sheets is 0.41 of the original value, and the results indicate that the same proportion of the total energy is abstracted from the α -particles in passing through successive layers. The abrupt falling-off of the photographic activity was found to correspond with the abrupt ceasing of the ionisation activity, and also with the phosphorescent action, and hence indicates that most probably photographic and phosphorescent effects are due to ionisation. The velocity of the α -particles on emission is only about 30 per cent. more than that at which ionisation effects cease, and this leads the author to make the interesting suggestion that probably similar disintegration of matter and emission of particles is taking place in many other kinds of matter, but that the velocity of the particles is too small to produce those electrical or photographic effects by which this emission has been detected.

L. M. J.

Secondary Radiation. JOHN A. McCLELLAND (*Sci. Trans. Roy. Dubl. Soc.*, 1905, [ii], 8, 169—182).—When the β and γ rays of radium are allowed to penetrate a substance, the latter emits a

secondary radiation of negatively charged particles. Comparison of the deflections in a magnetic field shows that the primary and secondary β -rays are similar in character. As a general rule, the substances of greater density produce the greater secondary radiation, but there are many exceptions to this rule. If elementary substances alone are considered, it is found that the intensity of the secondary radiation increases in all cases with the atomic weight of the substance.

J. C. P.

Secondary Radiation (Part II) and Atomic Structure. JOHN A. McCLELLAND (*Sci. Trans. Roy. Dubl. Soc.*, 1905, [ii], 9, 1—8).—The atomic weight appears to be the chief factor in determining the intensity of the secondary radiation exhibited by elementary substances (see preceding abstract). This point has been further tested, and the foregoing result confirmed for a large number of elements. It is further found that the secondary radiation increases less rapidly than the atomic weight. When the intensity of secondary radiation is plotted against atomic weight, a curve is obtained which shows the elements falling into well-marked divisions corresponding with Mendeléeff's periods. The curve flattens at the end of each period, and there is little increase of secondary radiation in passing from one period to the next. The view is adopted that the manner in which additional electrons are added on to form elements of greater atomic weight is different in passing from one period to the next from what it is in passing through elements not near the ends of a period.

J. C. P.

Properties of Radium in Minute Quantities. W. A. DOUGLAS RUDGE (*Phil. Mag.*, 1905, [vi], 10, 183).—A thin film produced on glass by the evaporation of a small quantity of solution of a radium preparation, in December 1903, is still as active as a week after preparation, although the quantity of radium present could not have been more than 0.000005 mg. (See Eve, this vol., ii, 367.)

L. M. J.

Simple Recognition of Helium from Radium Bromide. FRIEDRICH GIESEL (*Ber.*, 1905, 38, 2299—2300. Compare Abstr., 1903, ii, 20).—Two Geissler tubes of 5 and 15 c.c. capacity respectively, with aluminium electrodes, were charged each with 50 mg. of anhydrous radium bromide and evacuated as completely as possible, when the hydrogen and mercury lines were still prominent in the smaller but only faint in the larger tube. After two months the smaller tube exhibited the helium line $D_3 = \lambda 587.6$, and after six months the lines $\lambda 502$, $\lambda 495$, $\lambda 470$, and $\lambda 446$, the last three only faintly. So far the larger tube has exhibited only the line D_3 .

The helium spectrum was not diminished by prolonged passage of the induction current, and no alteration of the pressure in the tubes, as judged from the illumination, could be observed. As the activity of the gases in the tubes is much less than that of the gases obtained from radium solutions, the emanation must be retained by the anhydrous radium bromide.

G. Y.

Actinium and Emanium. WILLY MARCKWALD (*Ber.*, 1905, **38**, 2264—2266. Compare Debierne, *Abstr.*, 1904, ii, 223, 729; Giesel, *Abstr.*, 1904, ii, 462, 800; Hahn and Sackur, this vol., ii, 432).—The thorium (0.7 gram) precipitated from the chlorides of the noble earths (40 grams), obtained from the radium mother liquors, was strongly radioactive, the emanation exhibiting the rapid decay characteristic of actinium. The radioactive substance was not separated from the thorium on purification of this by solution in hydrochloric acid, precipitation as the oxalate, and conversion by heat into the oxide, but after some months the emanation ceases, the actinium losing its radioactivity. The cerium oxide and the mixture of didymium and lanthanum oxides obtained from the filtrate from the thorium are only slightly radioactive; the cerium oxide remains so, but the radioactivity of the didymium lanthanum oxide mixture increases as that of the thorium decreases. On dissolving the didymium lanthanum oxide mixture (18 grams) with 0.5 gram of inactive thorium oxide in hydrochloric acid and precipitating the thorium with sodium thiosulphate, the precipitate contains actinium whilst the didymium lanthanum oxides regained from the solution are only slightly radioactive.

Emanium and actinium are therefore not identical, but are genetically related: lanthanum \rightarrow emanium \rightarrow actinium. The names emanium and actinium would be more suitable if reversed, as it is the latter substance which yields an emanation. The author protests against the naming of such substances before they are thoroughly investigated.

G. Y.

Actinium and its Successive Products. T. GODLEWSKI (*Bull. Acad. Sci. Cracow*, 1905, 265—276; *Phil. Mag.*, 1905, [vi], **10**, 35—45).—Actinium behaves very similarly to thorium in its radioactive properties, producing an emanation which is transformed into an active deposit; this undergoes (1) a slow, rayless change, and (2) a rapid change. The author has applied to these actinium products the methods employed by Rutherford and Soddy in the case of the thorium products. The actinium compound was dissolved in hydrochloric acid and precipitated by ammonia: the precipitate was almost inactive; the residue from the filtrate was intensely active, but the activity decreased according to the exponential law, whilst the recovery curve for the precipitate was almost complementary. The active substance, termed AcX, does not immediately decrease, however, but first increases slightly, then afterwards falling to the half-value in 10.2 days, this resembling ThX. It was found that AcX gave out α -, β -, and γ -rays, and the author considers that the β -rays are in this case due to the actinium X itself and not solely to incited activity; in this respect it would differ from thorium X. The actinium X gives rise to an emanation with an exceptionally rapid rate of decay. This, as in the case of thorium, gives rise to three products, AcA, AcB, and AcC. The β -rays emitted by actinium are remarkable in being perfectly homogeneous and have less than half the penetrating power of those emitted by any other radio-element (compare *Abstr.*, 1904, ii, 223, 799).

L. M. J.

Radioactivity of the Bohemian Mineral Springs: Karlsbad, Marienbad, Teplitz-Schönau-Dux, and Franzensbad, and of St. Joachimsthal. HEINRICH MACHE and STEFAN MEYER (*Monatsh.*, 1905, 26, 595—625. Compare Mache, this vol., ii, 367).—The radioactive emanation obtained from the gases and waters of the springs in Karlsbad, Marienbad, Teplitz-Schönau-Dux, Franzensbad, and St. Joachimsthal is found to vary in amount between different springs in the same locality. Its rate of decay, as also that of the induced radioactivity, is the same as the rate of decay of radium emanation and of the activity induced by radium emanation. The presence of thorium could not be detected.

In Karlsbad, the cold ferruginous spring situated within the thermal sphere contains a greater proportion of radium emanation than the thermal springs, amongst which the radioactivity decreases with increasing temperature. In Teplitz-Schönau and in Franzensbad, the variation in amounts of emanation in the different springs is connected probably with the geological formation.

The waters from the St. Joachimsthal mines are highly radioactive, the amount of emanation increasing with the depth at which the spring is found. The lowest spring contains a larger proportion of radioactive emanation than has been found in any water previously examined.

In the springs evolving small amounts of gas, the ratio: *emanation in water, emanation in gas*: falls with the rise of temperature. As this ratio is much greater in the springs which give off large amounts of gas, the emanation in the gas must be derived from the water, an equilibrium being reached only in the former class of springs. G. Y.

"Thorium Activity" of Monazite. FRIEDRICH GIESEL (*Ber.*, 1905, 38, 2334—2336. Compare Sackur, this vol., ii, 367).—The "thorium activity" of monazite is not to be ascribed to the presence of thorium itself. The author has proved this by an examination of the radioactivity of the rare earths from monazite sand, when fractions which contained practically no thorium were found to be strongly radioactive. A. McK.

Some Radioactive Properties of Uranium. T. GODLEWSKI (*Phil. Mag.*, 1905, [vi], 10, 45—60).—It was shown by Rutherford (*Abstr.*, 1904, ii, 347), that if uranium is deprived of uranium X, the curves for increase of activity of the former and decay of activity of the latter are complementary, the half-value being reached in about 22 days. Meyer and Schweidler have found, however, that if uranium nitrate solution is shaken with ether, the ethereal solution contains no UrX, and the β -activity of this increases to half the total value in 22 days, but the crystals of uranium nitrate obtained from the aqueous solution lost β -activity at a different rate, decaying to half-value in 2 days. The cause of this behaviour has been investigated by the author, who shows it to be due to the fact that the UrX tends to remain in the mother liquor, and not to separate out with the crystals of the nitrate. One consequence of this is, that when any large crystals separate out from below in a solution, the upper surface of the crystal

is richer in UrX than the lower and exhibits a higher activity, but that the upper and lower activities tend to a constant value indicating a diffusion of the UrX through the crystals, even when the latter seem to be completely dry.

L. M. J.

Galvanic Cells produced by the Action of Light. MEYER WILDERMAN (*Proc. Roy. Soc.*, 1905, 74, 369—378. Compare Abstr., 1902, ii, 545).—A preliminary communication, dealing largely with the physico-mathematical theory of light cells, that is, cells in which one electrode is in the dark whilst the other is illuminated. The author has succeeded in elucidating the reactions and chemical equilibrium in light cells, including the phenomena of induction and deduction. It has been found that the total $E.M.F.$ in a light cell is due partly to increase of chemical potential and of solution pressure of the exposed electrode, and partly to a thermo- $E.M.F.$ caused by the one electrode being heated by the light. Both these $E.M.F.s$ are directly proportional to the intensity of the light and both give currents in the same direction. Hence it appears that light acts on the chemical potential and the solution pressure of the electrode in the same way as heat does.

J. C. P.

Ionic Velocities. S. TIJMSTRA (*Zeit. Elektrochem.*, 1905, 11, 249; HEINRICH DANNEEL, *ibid.*, 249—252).—Dempwolff (this vol., ii, 9) has found that the methoxyl ion in methyl alcohol has a velocity equal to that of the halogen ions. Tijmstra (Abstr., 1904, ii, 699) has shown that its velocity is greater than that of the hydroxyl ion. Danneel considers that the increase of the velocity of an ion in presence of undissociated molecules containing it is merely apparent. When an anion, for example, collides with the cation side of its parent molecule, it is supposed to remain combined, the displaced anion carrying on the electric charge. In this way the path which the ion has to traverse is shortened, and the transport of electricity apparently accelerated. It is shown that the apparent increase of the mobility of the ions of sodium and potassium chloride (Jahn, this vol., ii, 145) are possibly capable of explanation in this way.

T. E.

Dissociation of Electrolytes. CARL LIEBENOFF (*Zeit. Elektrochem.*, 1905, 11, 301—306).—An equation connecting the concentrations of the dissociated and non-dissociated parts of an electrolyte is deduced, partly from theoretical considerations which cannot be briefly abstracted. By means of it, the conductivity of dilute solutions of some salts are calculated with considerable accuracy.

T. E.

Electroaffinity of Anions. I. The Oxalate Ion. HANS SCHÄFER (*Zeit. anorg. Chem.*, 1905, 45, 293—323).—According to Abegg and Bodländer's method, the electroaffinity of the oxalate anion is ascertained from a study of the formation of double oxalates and from measurements of the ionic concentrations of the oxalates. The oxalate anion has a small electroaffinity as shown by the formation of numerous stable double oxalates and confirmed by the difficult solubility of most of the oxalates of the heavy metals. The paper contains

the following sections: (1) a review of the solubilities of oxalates and an account of the known double oxalates; (2) the double oxalates of copper; (3) the solubility of silver oxalate; its equilibrium with silver chromate; the dissociation of oxalic acid and its salts; (4) iron oxalates.

D. H. J.

Connection between Electrolytic Changes and the Temperature of the Electrodes. WILHELM MOLDENHAUER (*Zeit. Elektrochem.*, 1905, 11, 307—330).—The quantity of heat developed at an electrode is, according to Ostwald, the sum of the quantity of heat liberated by the chemical change at the electrode and the quantity of heat due to the passage of the electricity from the potential of the electrode to that of the electrolyte. These quantities are calculated for a number of typical cases from existing data. Experiments are then described in which the temperature of a tubular electrode is measured and also the temperature of the electrolyte, which is cooled by circulation of water in a coil. When the conditions of the experiment are kept constant, the difference of temperature between the electrode and the electrolyte is nearly proportional to the quantity of heat developed at the electrode. With sulphuric acid, the quantity of heat developed at the anode diminishes as the temperature of the electrode rises; at the same electrode temperature, it is nearly proportional to the current; it is least for acids containing from 2·4 to 9 per cent. of sulphuric acid. Less heat is developed with a platinised than with a smooth anode owing to the smaller potential difference. With strong acid the development of heat is sometimes very large for a short time owing to the formation of a layer of very concentrated acid of high resistance at the surface of the electrode. The observations are in qualitative agreement with the theory. At the cathode, a small absorption of heat is to be expected, and with platinised electrodes this was observed. Similar experiments are described with solutions of phosphoric and hydrochloric acids, potassium hydroxide, ammonium sulphate, and potassium chloride. With the latter, regular periodic variations in the heat developed at the anode were observed which are explained by changes in the nature of the electrolyte in contact with it, and corresponding changes in the chemical process going on there.

Further experiments deal with the influence of the anode temperature on the nature of the products formed. A hollow, suitably cooled platinum anode was used.

With sulphuric acid of sp. gr. $\leq 1\cdot45$, the yield of persulphuric acid is improved by cooling the anode to -2° , whilst with more concentrated acids it is diminished; these results seem to depend on the concentration of the HSO_4 ions present. In the preparation of ammonium persulphate or of potassium percarbonate, a small improvement in yield is obtained by cooling the anode to -2° . When a solution containing 20 per cent. of potassium chloride and 1 per cent. of potassium hydroxide is used, the yield of hypochlorite increases to a maximum as the anode temperature rises from 0 to 15° , falling off at higher temperatures, whilst the quantity of chlorate simultaneously formed increases steadily.

T. E.

Chemical Transfer of Metallic Potentials and the Chemical Solution Pressure of Metals. FRANZ FISCHER (*Zeit. physikal. Chem.*, 1905, 52, 55—88).—When external influences are excluded, the *E.M.F.* of certain open cells of the type metal | metallic salt solution | Pt slowly falls to zero, the same change taking place in a few hours if the contents of the cell are shaken. The metals for which this change has been observed are copper, mercury, and silver. Metals, on the other hand, such as zinc, at the other end of the electromotive scale, behave differently; the *E.M.F.* of a cell of the foregoing type falls off in this case until it assumes the value for the cell metal | metallic salt solution | hydrogen. Special examination of the cell Cu | copper sulphate | Pt shows that the change takes place at the platinum electrode only, and the view is adopted that cuprous sulphate is formed from the metallic copper and the copper sulphate, this in turn involving a tendency throughout the electrolyte to the separation of copper. The copper potential is thus transferred to the platinum electrode. The part played by the cuprous sulphate is illustrated by the fact that by the use of various solutions all saturated with cuprous sulphate the platinum can be made to assume any potential between that of oxygen and that of copper. That the *E.M.F.* of the cell Cu | copper sulphate | Pt falls off gradually is attributed to the formation of alloys of the two metals, these alloys becoming gradually richer in copper as the distribution of the cuprous sulphate through the electrolyte proceeds.

The observations recorded in the paper are connected with what is called the "chemical solution pressure" of the metals; by this term is meant, in contrast to "electrolytic solution pressure," a solution pressure in virtue of which a metal dissolves but without an accompanying electrical charge. A case in point is the reaction $\text{Cu} + \text{Cu}^{++} = 2\text{Cu}^+$. J. C. P.

Electromotive Behaviour of Copper and Zinc in their Solutions in Alkali Cyanides. FRITZ SPITZER (*Zeit. Elektrochem.*, 1905, 11, 345—368).—The differences of potential between copper and solutions of cuprous potassium cyanide, $\text{KCu}(\text{CN})_2$, containing various quantities of potassium cyanide and between zinc and solutions of zinc potassium cyanide, $\text{K}_2\text{Zn}(\text{CN})_4$, and potassium cyanide are measured. Considerable difficulty is experienced in obtaining constant values, especially in the case of copper. The solutions are all positive to the metals. Increase of the concentration of the copper or zinc salt or increase of the excess of potassium cyanide increases the potential difference, or, in other words, decreases the concentration of the metallic ions in the solution. Comparing solutions containing the same quantity of potassium cyanide, it is seen that the *P.D.* between zinc and a zinc solution is greater than that between copper and a copper solution, but the difference becomes smaller as the concentration of the cyanide increases; the influence of the concentration of the copper or zinc also diminishes so that in solutions containing about 2.5 gram mols. of potassium cyanide per litre, zinc and copper have about the same potential. In more concentrated cyanide solutions, copper has the higher potential.

Copper precipitates zinc from a solution of zinc potassium cyanide containing any excess of potassium cyanide, whilst zinc precipitates copper from solutions of potassium cuprous cyanide containing less than about 5 mols. of potassium cyanide solution per litre. The explanation of this apparently anomalous behaviour is that when zinc is precipitated by copper it combines with the copper, the compound having a very much smaller solution pressure than pure zinc.

This is proved by a number of experiments on the electrolysis of solutions of copper and zinc, cyanides dissolved in potassium cyanide solution. From such solutions, brass (with about 30 per cent. of zinc) is deposited at cathode potentials much below the potential of zinc in the solution.

The deposition of both copper and zinc from these solutions takes place with difficulty, so that when the current density is increased the potential of the cathode increases quickly and the value required for the liberation of hydrogen is soon reached. For this reason, no metal is deposited from solutions containing a large excess of potassium cyanide.

The numerical results of the experiments are given in the form of tables. T. E.

Dissociation of Ternary Electrolytes. GOTTFRIED KÜMMELL (*Zeit. Elektrochem.*, 1905, 11, 341—343. Compare this vol., ii, 226).—Replying to the criticisms of Drucker (this vol., ii, 371), the author shows that the depression of freezing point produced by a mixture of magnesium and potassium chlorides is almost equal to the sum of the depressions of the separate salts. Hence it is probable that complex ions are not formed from these salts. The *E.M.F.s* of cells consisting of two calomel electrodes, one with potassium or sodium chloride, the other with magnesium chloride solution, are shown to be 0.004 and 0.002 volt respectively when the solutions are isohydric. This confirms the view that the concentrations of the chlorine ions in these isohydric solutions are the same, the small *E.M.F.s* observed being due to the different mobilities of the Na^+ or K^+ ions and the MgCl^+ ions.

Drucker's method, based on the depression of freezing point, is only exact when applied to very dilute solutions. It has also the disadvantage of giving the ionic concentrations only at the freezing point, and is therefore unsuitable for electrolytes the dissociation of which is much affected by temperature. T. E.

Hall Effect of Bismuth at High Temperatures. HEINRICH FRH. RAUSCH VON TRAUBENBERG (*Ann. Physik*, 1905, 17, 78—103).—The Hall effect was investigated with three plates of bismuth, and the variation with temperature determined from ordinary temperatures to the melting point. The Hall rotation coefficient was found to decrease with temperature, the value falling at first rapidly but at a decreasing rate until about 260° , after which the fall is rapid to the melting point. L. M. J.

Influence of Concentration on the Magnetic Properties of Solutions of Cobalt. P. VAILLANT (*Compt. rend.*, 1905, 140, 1632—1634).—Measurements were made with solutions of the chloride, sulphate and nitrate of cobalt, using Becquerel's torsion method of observation. The results show that the specific coefficient (k) varies little with the nature and concentration of the acid group, and that it diminishes as the concentration of the salt in the solution increases. This variation in the value of k appears to be due to ionisation. The values of c and c' , the specific coefficients of dissociated and undissociated molecules of the salt respectively, are discordant in the cases of solutions of the sulphate and the chloride. These irregularities are probably due to the formation of different hydrates (compare Abstr., 1903, ii, 254), since the values become more concordant as the solutions become more dilute and, *pari passu*, the hydration becomes stationary.

T. A. H.

Physical Properties of an Extensive Series of Alloys of Iron. IV. Thermal Conductivity. V. Micro-structure. W. FLETCHER BARRETT, W. BROWN, and ROBERT A. HADFIELD (*Sci. Trans. Roy. Dubl. Soc.*, 1904, [ii], 8, 109—126. Compare Barrett, Abstr., 1902, ii, 377).—Uniform rods made of the alloys were covered with a thin coating of paraffin wax; the length of wax melted in each case, after one end of the rod had been kept for a long time at a high, steady temperature, was measured. The thermal conductivities of any two rods are then proportional to the squares of the lengths of wax melted in each case. The results obtained in this way were confirmed generally by another and more accurate method in which the temperature gradient in each rod was determined by means of thermocouples lashed on to the rod.

The thermal conductivity (as also the electrical conductivity) of iron is lowered by carbon and manganese, the drop being most marked for the first small additions. Nickel also lowers the thermal and electrical conductivities of iron, but to a much smaller extent than the same percentage of carbon or manganese. So far, tungsten has the least effect of any single element in reducing the thermal conductivity of iron; aluminium has the greatest effect. The highest thermal and electrical resistivity has been found in the case of an alloy containing 69.36 per cent. of iron, 25 per cent. of nickel, and 5.04 per cent. of manganese. It is noteworthy that of a series of steel alloys containing copper, none had a higher thermal or electrical conductivity than the iron taken as standard. These alloys, however, contained impurity in the shape of carbon or manganese, both of which tend to lower the conductivity. At the same time, it is considered probable that copper would have very little effect on the conductivity of pure iron. Thermal conductivity, like electrical conductivity, is increased by annealing.

Compared with copper, the electrical conductivity of iron and its alloys is throughout lower than their thermal conductivity. When the conductivity is plotted against the percentage of the added element, the general trend of the curves for any one series of alloys is the same thermally and electrically. The curve obtained by taking

thermal conductivities as ordinates and electrical conductivities as abscissæ is fairly smooth and of parabolic form, except when the conductivities are very low, in which case the curve becomes much steeper.

It has been shown previously by the authors that a small percentage of silicon or aluminium alloyed with iron raises the magnetic permeability beyond that of the purest commercial iron, whilst a sufficient addition of manganese, itself feebly magnetic, renders iron practically non-magnetic. It was suggested that silicon or aluminium, combining with oxygen or dissociated gas, may free the iron from oxide or give it a closer texture, and thus raise its magnetic permeability. A study of the microstructure of some alloys has accordingly been made at the National Physical Laboratory, and the results of this study are in harmony with the foregoing suggestion. J. C. P.

Calorimetric Methods, especially referring to the Determination of the Heat of Combustion of Organic Compounds. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 140, 1497—1504).—An historical *résumé* of the work done by the author and others on heats of combustion; polemical in reply to Thomsen (compare this vol., ii, 231 and 435). M. A. W.

Determination of Specific Heats of Solutions. Molecular Heats of Good and Bad Electrolytes. PAUL TH. MÜLLER and C. FUCHS (*Compt. rend.*, 1905, 140, 1639—1641).—A constant electric current is passed for a definite length of time through a hollow glass spiral filled with mercury and wholly immersed in the solution the specific heat of which is to be measured. The resultant change of temperature of the solution is observed, and from this and the usual data its specific heat (c) is calculated. The molecular heat of the solution is equal to $(M + 18n)c$, where M is the molecular weight of the salt, n the number of molecules of water in which M is dissolved, and c the specific heat of the solution.

The molecular heat of the solution diminishes as the concentration of the solute decreases, and may even become negative in the case of good electrolytes, but with poor electrolytes change of concentration produces little or no variation in the value of this constant. This difference is explained by the assumption that the variation in the value of the molecular heat is due to change in the state of hydration, and that ionised substances exhibit a greater facility for undergoing hydration than un-ionised substances (compare Berthelot, *Mécanique chimique*, 1879, i, 508; Puschl, *Abstr.*, 1901, ii, 224; and Jones and Getman, *Abstr.*, 1904, ii, 386). T. A. H.

Mercury Formates. RAOUL VARET (*Compt. rend.*, 1905, 140, 1641—1643).—By observing the heat changes involved in reactions between mercurous formate and potassium iodide alone and in presence of iodine, the value 175.1 Cal. was obtained for the heat of formation of solid mercurous formate. The heat of formation of solid mercuric formate was found to be 161.5 Cal. by means of measurements of the heat developed by the solution of mercuric oxide in

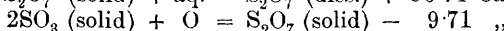
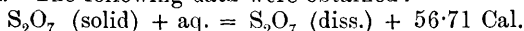
formic acid. The decomposition of mercuric formate into mercurous formate, formic acid, and carbon dioxide develops 53.2 Cal.; and into liquid mercury, liquid formic acid, and carbon dioxide, 20.7 Cal. The solution of mercuric formate in formic acid develops 1.8 Cal.

T. A. H.

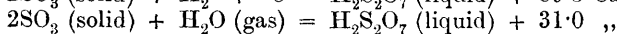
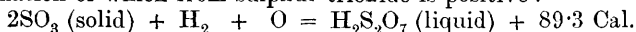
Thermochemistry of Neodymium. CAMILLE MATIGNON (*Compt. rend.*, 1905, 141, 53—55).—The heat of formation of the reddish-brown form of neodymium sulphide, Nd_2S_3 , is 285.9 Cal., that of the anhydrous chloride 249.5 Cal., of the hydrated chloride, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, 268.9 Cal., of the anhydrous iodide 157.7 Cal., of the anhydrous sulphate 928.2 Cal., and of the hydrated salt, $\text{Nd}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 8\text{H}_2\text{O}$, 946.8 Cal. These values indicate that neodymium and the related elements, so far as chemical affinity is concerned, occupy a place between the alkali metals and magnesium.

T. A. H.

Combustion of Sulphur in the Calorimetric Bomb. H. GIRAN (*Compt. rend.*, 1905, 140, 1704—1707).—The fact that the heat developed by the combustion of sulphur in the calorimetric bomb increases with the pressure has been previously supposed by the author to be due to the formation of increasing quantities of persulphuric anhydride (compare this vol., ii, 76). This hypothesis is now shown to be untenable, for, according to calorimetric measurements, heat is absorbed when persulphuric anhydride is formed from sulphur trioxide and oxygen. The following data were obtained:



After the combustion of sulphur in the bomb, a viscous liquid of light-brown colour remained which evolved nitrous fumes on contact with water. This was found to be pyrosulphuric acid containing acid nitroxyl sulphate in solution, the formation of which was due to the presence of nitrogen in the oxygen used in the experiments. When the liquid was heated, it evolved sulphur trioxide, and the acid nitroxyl sulphate separated in crystalline form. It is calculated that the small proportion of hydrogen present in the oxygen used was sufficient to convert all the sulphur trioxide formed into pyrosulphuric acid, the heat of formation of which from sulphur trioxide is positive:



These exothermic changes are now regarded as the cause of the increase of the heat of combustion of sulphur with increasing pressure.

H. M. D.

Heats of Solution and of Dilution. RUDOLF WEGSCHEIDER (*Monatsh.*, 1905, 26, 647—662. Compare Stackelberg, *Abstr.*, 1898, ii, 498).—Equations are given for the relationships between the various heats of solution and of dilution, which permit of these being calculated from the total heat of solution; this being represented as a function of the volume of water, and to be derived from the heat of dissolution in a solution with the aid of the heat of dilution. The method of calculation and the accuracy obtainable, especially for the

infinitesimal heat of solution, are exemplified in the case of sodium carbonate and nitrate and potassium chlorate. G. Y.

Apparatus for the Determination of the Specific Gravity of Solid Substances in Powder or in a Granular Form. J. von WROCHEM (*Chem. Centr.*, 1905, i, 1577—1578; from *Mitt. Techn. Vers.-A. Berlin*, 22, 217—220).—The original paper contains a critical account of the apparatus of Schumann, Suchier, Beck and Erdmenger, and Mann, with reference to their use for cement. A modification of the last-named apparatus is sketched and described in the abstract.

The measuring tube is connected with a flask by means of an india-rubber bung with two holes. The lower portion of the tube passes through one hole and reaches to the bottom of the vessel. In the second hole a T piece is fitted, one limb of which is attached to a rubber pressure ball, whilst by means of the other the apparatus may be filled or any excess of pressure relieved. A glass tap in the lower portion of the measuring tube just above the bung of the flask serves to connect or separate the two vessels, and between this and the cooling jacket which surrounds the measuring tube a side tube with a tap is attached through which the measuring flask is filled. In a newer form, an automatic adjusting arrangement similar to that of a Zahn burette is attached in place of the side tube. The measuring tube has a capacity of 50 c.c. and is graduated below the bulb from 0 to 15 c.c. in 1/20 c.c. The whole apparatus is mounted on suitable stands. E. W. W.

Densities of Carbon Dioxide, Ammonia, and Nitrous Oxide. PHILIPPE A. GUYE and ALEXANDRE PINTZA (*Compt. rend.*, 1905, 141, 51—53. Compare Abstr., 1904, ii, 812).—The carbon dioxide was prepared by heating sodium hydrogen carbonate. It was weighed by absorption in a strong solution of potassium hydroxide. The ammonia was obtained from commercial liquid ammonia and was freed from amines by passing it over red-hot lime and then converting it into the chloride, recrystallising this and regenerating the ammonia, which was dried over potassium hydroxide contained in soda-glass vessels. It was weighed by absorption in charcoal.

The mass of 1 litre of carbon dioxide was found to be 1.9768 grams, of ammonia 0.7708 gram, and of nitrous oxide 1.9774 grams. These values for carbon dioxide and nitrous oxide agree within the limits of experimental error with those found by Rayleigh, but the value found for ammonia is considerably lower than that (0.7719) observed by Leduc. Comparison of the values found for nitrous oxide and carbon dioxide by the method recently described (this vol., ii, 442) leads to the figure 14.007 for the atomic weight of nitrogen, and the application of the same method to those found for nitrogen and carbon monoxide to the value 14.006 for this constant. T. A. H.

Expansion and Density of some Gases at High Temperatures: Application to the Determination of their Molecular Weights. ADRIEN JAQUEROD and F. LOUIS PERROT (*Compt. rend.*, 1905, 140, 1542—1544).—Using a nitrogen thermometer (compare

this vol., ii, 10), the authors have measured the coefficient of expansion between 0° and 1067° of some of the common gases, and the results are appended :

Gas.	Initial pressure at 0° .	Coefficient of expansion at constant volume between 0° and 1067° .
Air.....	230 mm.	0.003,6643
Oxygen	180—230 „	0.003,6652
Carbon monoxide...	230 „	0.003,6648
Carbon dioxide	{ 240 „	0.003,6756
	{ 170 „	0.003,6713

The corresponding value for nitrogen, calculated from the experimental value between 0° and 100° (0.003,6650), is the same as that of air. The molecular weights of the gases at 1067° , calculated from their densities at that temperature, are—nitrogen 28.0155, carbon monoxide 28.009, and carbon dioxide 43.992 ($O_2 = 32$). M. A. W.

Osmotic Experiments on Mixtures of Alcohol and Water.

P. S. BARLOW (*Phil. Mag.*, 1905, [vi], 10, 1—12).—Pickering has described an experiment which he considered a conclusive proof of the existence of hydrates in solution. A mixture of propyl alcohol and water is separated from water by a semi-permeable membrane and exhibits an increase of osmotic pressure, but a similar increase is obtained if the cell containing the mixture is placed in propyl alcohol. The contention of Pickering, therefore, was that the membrane is permeable to either the alcohol or water, but not to the complex hydrated molecules. The author has repeated the experiment with methyl, ethyl, and propyl alcohols, and finds, as stated, that an increase of osmotic pressure results, but that this is only temporary, and that after a maximum value has been obtained the pressure falls steadily and permanently. His experiments indicate that this fall is due to the liquid present in the walls of the porous pot which does not become displaced and does not reach a new equilibrium until a short time after being placed in a new liquid. L. M. J.

Different Forms and Transformations of the Boundary Curves in the case of Partial Miscibility of Two Liquids.

JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 636—646).—A continuation of the earlier paper (this vol., ii, 234). J. C. P.

Exact Expression for the Course of the Spinodal Curves and of their Plait Points for all Temperatures, in the case of Mixtures of Normal Substances. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 646—657).—A theoretical paper. J. C. P.

Shape of the Plait-point Curve for Mixtures of Normal Substances. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 33—48).—A continuation of the earlier communication (preceding abstract). J. C. P.

Phase Rule. RUDOLF WEGSCHEIDER (*Zeit. physikal. Chem.*, 1905, 52, 171—184. Compare Abstr., 1903, ii, 356; 1904, ii, 112, 389).—A theoretical paper. J. C. P.

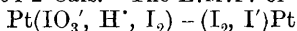
Some Determinations in the Systems: $\text{KIO}_3\text{—HIO}_3\text{—H}_2\text{O}$, $\text{NaIO}_3\text{—HIO}_3\text{—H}_2\text{O}$, and $\text{NH}_4\text{IO}_3\text{—HIO}_3\text{—H}_2\text{O}$. PIETER A. MEERBURG (*Zeit. anorg. Chem.*, 1905, 45, 324—344).—In order to determine the exact conditions under which potassium di-iodate is formed at a definite temperature from aqueous solutions of its components KIO_3 and HIO_3 , the ternary system $\text{KIO}_3\text{—HIO}_3\text{—H}_2\text{O}$ has been investigated at 30° , and for comparison the isotherms for the same temperature in the case of the systems $\text{NaIO}_3\text{—HIO}_3\text{—H}_2\text{O}$ and $\text{NH}_4\text{IO}_3\text{—HIO}_3\text{—H}_2\text{O}$ have been determined; the "residue method" of the previous communication (Abstr., 1904, ii, 112) was employed.

For the system $\text{KIO}_3\text{—HIO}_3\text{—H}_2\text{O}$, the original paper gives the exact conditions for the formation of the known binary compounds, $\text{KIO}_3\text{,HIO}_3$ (di-iodate) and $\text{KIO}_3\text{,2HIO}_3$ (tri-iodate), from their components. It is possible to crystallise potassium di-iodate from pure water at 30° ; hence, when the tri-iodate is crystallised at this temperature, the product may contain the labile form of the di-iodate.

In the system $\text{NaIO}_3\text{—HIO}_3\text{—H}_2\text{O}$, it is found that, contrary to Blomstrand's statement (Abstr., 1890, 107), the tri-iodate $\text{NaIO}_3\text{,2HIO}_3$ is anhydrous, and that, contrary to Penny's statement, the salt $\text{NaIO}_3\text{,HIO}_3$ does not exist, but instead the pyro-compound $\text{Na}_2\text{O,2I}_2\text{O}_5$. This pyro-salt is slowly formed from certain definite proportions of the three components.

In the system $\text{NH}_4\text{IO}_3\text{—HIO}_3\text{—H}_2\text{O}$, only the known ammonium tri-iodate is obtained. The di-iodate is not capable of existence at 30° . D. H. J.

Chemical and Electrical Examination of the Equilibria: $\text{HIO}_3 + 5\text{HI} \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$ and $\text{HBrO}_3 + 5\text{HBr} \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$. ROBERT LUTHER and G. V. SAMMET (*Zeit. Elektrochem.*, 1905, 11, 293—295).—In acid solutions the equilibrium $\text{HIO}_3 + 5\text{HI} \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$ leads to the formation of the substances on the right hand, those on the left being formed in alkaline solutions. In a solution saturated with sodium borate and boracic acid, which contains 6.5×10^{-7} mols. H^+ at 25° , the concentrations of all the substances are measurable analytically, but equilibria between iodine and water and hydriodic acid and oxygen, the constants of which are unknown, interfere with the measurement. The concentrations of the I' and IO_3' ions may, however, be made constant by shaking a solution of iodine with solid silver iodide and iodate. Equilibrium is attained in about 7 weeks at 25° or in 4 days at 60° . The values of the equilibrium constant $K = [\text{H}']^6[\text{IO}_3']/[\text{I}']^5[\text{I}_2]^3$ are 2.8×10^{-47} at 25° and 5.2×10^{-42} at 60° . From these values the heat of the reaction $\text{HIO}_3 + 5\text{HI} + \text{aq} = 3\text{I}_2(\text{dissolved}) + \text{aq}$ is calculated to be 68.3 Cals.; thermochemical experiments give 64.2 Cals. The *E.M.F.* of the cell



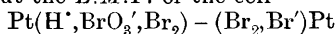
is 0.549 volt at 25° , the value calculated from the equilibrium constant above given being 0.5493 volt.

The *E.M.F.* of the iodate-iodine electrode was measured against the calomel electrode and found to vary with the concentrations of H^+ , IO_3' and I_2 in the way required by the theoretical equation $E(\text{electrode}) - E(\text{drop electrode}) = E_o + (RT/10F) \log([H^+]^{12} [IO_3']^2 / [I_2])$. This is the first case in which the theoretical connection between the *E.M.F.* and the concentrations of *three* different substances has been found to hold good quantitatively. The value of E_o at 25° is 1.454 volts.

In connection with the above measurements, the solubility of iodine in water was found to be 0.001341 gram mol. per litre at 25° and 0.00416 gram mol. per litre at 60° , from which its molecular heat of solution is -6.37 Cals. The solubility of silver iodide at 60° is 1.08×10^{-7} gram mols. per litre.

The solubility of silver iodate at 25° and 60° is 2.16×10^{-4} and 6.54×10^{-4} gram mols. per litre, and its heat of precipitation 12.5 Cals. The electrical conductivities of sodium iodate, nitric and iodic acids at 25° and 60° are also given.

The equilibrium $\text{HBrO}_3 + 5\text{HBr} \rightleftharpoons 3\text{Br}_2 + 3\text{H}_2\text{O}$ could not be determined chemically, but the *E.M.F.* of the cell



was found to be 0.393 volt at 25° . From this figure the equilibrium constant at 25° $[H^+]^6 [\text{BrO}_3'] [\text{Br}']^5 / [\text{Br}_2]^3 = 7.3 \times 10^{-34}$.

The *E.M.F.* of the bromic acid - bromine electrode follows a formula similar to that above given for iodine, the constant $E_o = 1.764$ volt at 25° .
T. E.

Hydration in Solution. GILBERT N. LEWIS (*Zeit. physikal. Chem.*, 1905, 52, 224—230).—The author criticises adversely Jones and Getman's method of estimating quantitatively the degree of hydration in a salt solution (Abstr., 1904, ii, 710), mainly because it leads in many cases to the result that the degree of hydration increases with the concentration of the solute (see also Biltz, Abstr., 1904, ii, 710). At the same time Jones and Getman's experimental work is considered to be valuable because it indicates the probable relative hydration for different salts.

The author has made some experiments on the colour changes shown by solutions of cobalt chloride, copper chloride and bromide, and considers that these colour changes are associated with the varying degree of hydration of these salts.

[*Note by Abstractor.*—The author makes no reference to the recent paper by Donnan and Bassett (Trans., 1902, 81, 939) dealing with the colour changes shown by the chlorides of cobalt and other metals.]

J. C. P.

Influence of Temperature on the Amount of Water of Crystallisation as Evidence supporting the Theory of the Existence of Hydrates in Solution. HARRY C. JONES and H. P. BASSETT (*Zeit. physikal. Chem.*, 1905, 52, 231—235).—The earlier work (Jones and Getman, Abstr., 1904, ii, 235, 386, 710) has indicated the existence of hydrates in salt solutions, the stability

of these hydrates diminishing as the temperature rises. The latter phenomenon is now correlated with the well-known general fact that the number of molecules of water with which a salt crystallises from water diminishes as the temperature rises.

The fact that a concentrated solution of cobalt chloride turns blue when shaken with crystallised calcium chloride is attributed to the dehydration of the cobalt chloride. The conclusion is drawn that a salt (calcium chloride in the foregoing special case) can combine in solution with more molecules of water than it can carry with it out of the solution in the form of water of crystallisation (see, however, Donnan and Bassett, *Trans.*, 1902, 81, 939). J. C. P.

Solubilities in Mixtures of Solvents. II. WALTER HERZ and M. KNOCH (*Zeit. anorg. Chem.*, 1905, 45, 262—269. Compare *Abstr.*, 1904, ii, 709).—The solubilities were determined at 25° as described in the former paper.

(I.) Determinations of Solubility in Mixtures of Acetone and Water.—Potassium bromide is almost insoluble in pure acetone; in aqueous acetone its solubility varies in a similar manner to that of potassium chloride.

Ammonium chloride behaves like sodium chloride. With mixtures of acetone varying from 46.5 pts. of acetone (by volume) and 53.5 pts. of water to 85.7 pts. of acetone and 14.3 pts. of water, the addition of ammonium chloride causes the formation of two layers.

Sulphur is slightly soluble in acetone; its solubility is less in presence of water at 25°. Bodländer suggested that the quotient $W/\sqrt[3]{S}$ is a constant for solutions in aqueous alcohol (W being the number of grams of water and S the number of grams of the dissolved substance in 100 c.c. of the mixed solution). The results of the present paper show that Bodländer's formula is applicable to sugar, ammonium chloride, or sulphur, but not to barium chloride or potassium bromide in solution in aqueous acetone.

(II.) Solubilities in Aqueous Alcohol.—Mercuric iodide was chosen as a substance sparingly soluble in water but easily soluble (1.754 pts. at 25°) in alcohol. Bodländer's formula (which is here of the form alcohol / $\sqrt[3]{S}$, since the alcohol and not the water is the constituent which promotes solution) appears to be applicable.

(III.) Solubilities in Aqueous Glycerol.—In the case of succinic acid, potassium bromide, potassium chloride, sodium chloride, and ammonium chloride, the solubility diminishes as the percentage of glycerol increases. The conditions for the application of Bodländer's formula are not obtained, as the solubility of the above substances in pure glycerol is not inconsiderable.

The solubility of boric acid in aqueous glycerol changes little up to 7 per cent. of glycerol or more, but as the percentage of glycerol is still further increased the solubility rapidly becomes greater, probably owing to the formation of a complex of boric acid and glycerol.

The solubility of iodine in glycerol is small, but much more considerable than in water. Bodländer's formula is approximately applicable.

D. H. J.

Reactions which take place in Several Stages. ERICH BRUNNER (*Zeit. physikal. Chem.*, 1905, 52, 89—96. Compare Jungius, Abstr., 1904, ii, 716).—A theoretical paper in which is considered the application of the law of mass action to chemical changes involving the formation, or the possible formation, of an intermediate compound. For a chemical change which can be analysed into two partial processes or stages, it is impossible to deduce anything as to the relative velocity of the two component reactions from the two corresponding equilibria.
J. C. P.

Nuclear Synthetical Equilibrium between Phenols, Bicarbonates, and Phenolcarboxylic Acids in Aqueous Solution. JOH. A. AF HÄLLSTRÖM (*Ber.*, 1905, 38, 2288—2290. Compare Skraup, Abstr., 1890, 136).—If phloroglucinol and potassium hydrogen carbonate or phloroglucinol and potassium phloroglucinolcarboxylate are dissolved in water through which a current of oxygen-free carbon dioxide is passed, after some days at 50° a state of equilibrium is reached between phloroglucinol, potassium phloroglucinolcarboxylate, and potassium hydrogen carbonate. The equilibrium is represented by the formula

$$\frac{\text{Phl} \cdot \text{H} \times \text{HCO}_3'}{\text{Phl} \cdot \text{CO}_2'} = \frac{\text{Phl} \cdot \text{H} \times a' \text{KHCO}_3}{a'' \text{Phl} \cdot \text{CO}_2 \text{K}} = \text{constant},$$

where $\text{Phl} = \text{C}_6\text{H}_2(\text{OH})_3$, and a' and a'' are the degree of dissociation of the potassium salts. In eight experiments, assuming a' and a'' to be approximately the same, the constant was found $= 0.115 \pm 0.015$.

G. Y.

Hydration and Hardening. PAUL ROHLAND (*Zeit. Elektrochem.*, 1905, 11, 338).—A reply to Jordis (this vol., ii, 155).
T. E.

Autocatalysis and the Transformation of γ -Hydroxy Acids, with and without Addition of other Acids, conceived as an Ionic Reaction. ARIE W. VISSER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 760—769).—If it is supposed that the change in intensity of the catalyst with the change in concentration of the reacting substance is constant, then $-dI/dC = k_2$, whence $I = k_1 - k_2 C$. The equation for unimolecular reaction, when the intensity of the catalyst is taken into account, is $-dC/dt = kCI$, which for the particular case referred to becomes $-dC/dt = k(k_1 - k_2 C)C$.

Using the experimental data obtained by Henry (Abstr., 1892, 1303), the author shows that the transformation of γ -hydroxy-acids into their lactones may be satisfactorily represented as being a reaction between the positive and negative ions.
J. C. P.

Theory of Colloids. HEINRICH BECHHOLD (*Zeit. Elektrochem.*, 1905, 11, 339—340).—A reply to Jordis (this vol., ii, 447).
T. E.

Osmotic Pressure of Colloidal Solutions. JACQUES DUCLAUX (*Compt. rend.*, 1905, 140, 1544—1547).—The granules of a colloidal solution may be regarded as ions of a large size in that they are conductors of electricity (compare this vol., ii, 432), and exert a specific osmotic pressure which can be measured by placing the

solution in a vertical cylinder with collodion walls and measuring the difference between the levels of the internal and external liquid after diffusion has occurred. The ratio between the osmotic pressure and the electrolytic conductivity of colloidal solutions of different concentrations is not constant, because the properties of the granules of such solutions vary with their concentration.

M. A. W.

Equilibrium between Proteids and Electrolytes. I. Equilibrium in the System Egg-albumin, Ammonium Sulphate, and Water. GINO GALEOTTI (*Zeit. physiol. Chem.*, 1905, 44, 461—471. Compare Abstr., 1904, i, 355).—The precipitation of egg-albumin by ammonium sulphate is a completely reversible process. The precipitation begins when the concentration of the salt has reached a certain limit, and the addition of more saturated sulphate solution produces further precipitation until with a completely saturated solution no albumin remains in solution. The addition of water causes the albumin to redissolve. The various precipitates obtained by fractional precipitation have the same composition. The crystalline needles and globulites obtained by evaporating a clear solution of albumin and ammonium sulphate consist of pure albumin.

The points of equilibrium are represented by means of isothermals in a triangle.

When an albumin solution is mixed with a certain quantity of saturated ammonium sulphate solution a precipitate appears only after some time, and thus a system in labile equilibrium is formed which exists for some time as a clear solution and then separates into two phases. This system has also been represented by isotherms.

J. J. S.

Solid Peptone Membranes on a Water-surface, and the Cause of their Formation. WILMOT V. METCALF (*Zeit. physikal. Chem.*, 1905, 52, 1—54. Compare Ramsden, Abstr., 1904, ii, 323).—When a drop of a peptone solution is allowed to fall on water, it spreads itself completely over the free water-surface and over the moistened walls of the containing vessel, forming a fine membrane which is stronger at 0° than at 18° and increases in strength up to a certain point as time goes on. A drop of the peptone solution cannot, however, spread itself over dry glass. A membrane obtained in the aforementioned manner has the same properties whether it is formed in an atmosphere of oxygen or of hydrogen, and it allows the free evaporation of the water below. An already-formed membrane which is fairly strong does not expand noticeably when brought into contact with a fresh water-surface, although an expansion may be detected when the membrane is weak. The minimum quantity of peptone required for the formation of a solid membrane is about 4×10^{-7} grams per square centimetre. It has been shown that a well-defined solid membrane can be formed also from a pure peptone compound. The surface tension of peptone solutions diminishes as the concentration increases. Various hypotheses relating to the observed phenomena are discussed, and the view is adopted that the peptone membranes are an

experimental realisation of Gibbs' thermodynamical principle, according to which a chemical change may be caused by surface tension.

J. C. P.

Formation of Structures in Jellies. HEINRICH BECHHOLD (*Zeit. physikal. Chem.*, 1905, 52, 185—199).—The paper deals with the phenomena of intermittent precipitation studied by Liesegang, Morse and Pierce (Abstr., 1904, ii, 14), and Hausmann (*ibid.*, 547). The reaction specially considered is the precipitation of silver nitrate by ammonium chromate or dichromate, and it is shown that silver chromate is slightly soluble in ammonium chromate and in the ammonium nitrate formed. If then silver nitrate is allowed to diffuse into a jelly containing ammonium chromate, the ammonium nitrate produced in the first precipitation zone will have an effect in preventing the precipitation of more silver chromate in its immediate neighbourhood. Only in a region in which the concentration of ammonium nitrate has sufficiently fallen off will fresh precipitation of silver chromate take place. Other factors also may be concerned in the observed intermittent precipitation, as, for example, the power of ions to promote or hinder the precipitation of suspensions or colloidal solutions, the manner in which the setting point of the gelatin is affected by the diffusion into it of the various salts, and the ability of colloids to precipitate each other only when mixed in certain proportions.

J. C. P.

Influence of Electrolytes on the Mutual Precipitation of Colloids of Opposite Electrical Sign. LARGUIER DES BANCELS (*Compt. rend.*, 1905, 140, 1647—1649).—By means of a series of experiments with such "couples" of colloids as colloidal ferric hydroxide (positive) with aniline-blue (negative), and colloidal arsenic sulphide (negative) with methyl-violet (positive), the author has found that the mutual precipitation of colloids of opposite sign is partially inhibited by the previous addition of an electrolyte, that the precipitate formed by the mixture of solutions of two such colloids is dissociated by the addition of an electrolyte capable itself of precipitating one of the reacting colloids, and finally, that when an electrolyte is added to a solution of a colloid (*a*) which it does not precipitate, and to the mixture a second colloid (*b*) of opposite sign is added, precipitation always takes place. With small quantities of electrolyte present, the precipitate is a mixture of *a* and *b*; with larger quantities of electrolyte, it consists of *b* alone; and if the quantity of electrolyte is again increased, both *a* and *b* are again precipitated.

T. A. H.

Miscibility in the Solid State, and Isomorphism, in the case of Carbon Compounds. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 7, 658—666).—In recent years it has been shown that many organic substances yield mixed crystals and solid solutions, but it is not permissible to draw conclusions as to existing isomorphism solely from the course of the melting or solubility curves for two components. It is accordingly thought desirable to investigate thoroughly the miscibility and crystallographic relationship of pairs

of organic substances, and in this communication the author deals with *p*-nitrodiethylaniline and *p*-nitrosodiethylaniline (compare Bruni and Callegari, *Abstr.*, 1904, ii, 545). It is found that these two compounds are completely isomorphous and also completely miscible in the solid state.

J. C. P.

Fundamental Laws of Stoichiometry and the Atomic Theory. The Faraday Lecture by W. Ostwald. RAFFAELLO NASINI (*Memor. R. Accad. Lincei*, 1905, [v], 5, 119—153).—This memoir contains a criticism of the views of Ostwald expressed in his Faraday Lecture (*Trans.*, 1904, 85, 506—522), and is unsuitable for abstraction.

T. H. P.

Periodic Classification of the Elements. ALFRED WERNER (*Ber.*, 1905, 38, 2022—2027).—A reply to Abegg (this vol., ii, 380). In the periodic classification of the elements, Abegg's conception of choosing the periods to be double or several times eight cannot be accepted. The system must be based on the periods as differentiated by the atomic volume curve.

A. McK.

Periodic Classification of the Elements. RICHARD ABEGG (*Ber.*, 1905, 38, 2330—2334).—A reply to Werner (preceding abstract).

A. McK.

New Forms of Lecture and Laboratory Apparatus. GEORGE B. FRANKFORTER and FRANCIS C. FRARY (*J. Amer. Chem. Soc.*, 1905, 27, 744—747).—Certain forms of apparatus suitable for lecture and laboratory purposes are described for (a) the determination of the hydrogen equivalent of zinc, (b) the preparation of sulphuric acid, and (c) the demonstration of Charles' law. For details, the description and diagrams in the original must be consulted.

E. G.

New Apparatus. S. P. BEEBE and B. H. BUXTON (*Amer. J. Physiol.*, 1905, 14, 7—11).—Some pieces of laboratory apparatus (an automatic compressed air and vacuum apparatus, a centrifuge, a drying apparatus, and an electric water-bath) are described and figured.

W. D. H.

A New Form of Test-tube. EDUARD SCHAEER (*Zeit. anal. Chem.*, 1905, 44, 396—397).—The tube described is of Jena glass, and is 17 mm. in diameter and 120 mm. in height. The lower end is widened out to a diameter of 28 mm. and the bottom is flat, so that the tube will stand upright. The tube will bear heating, and is suitable for a variety of operations.

W. P. S.

Two Modifications of the Töpler Mercury Air Pump. ALFRED STOCK (*Ber.*, 1905, 38, 2182—2185).—Two new modifications of the Töpler pump are described and figured; they have the advantage of being small and easily transported, they work quickly and easily, the mercury does not come into contact with india-rubber or fat, and so keeps clean; whilst, lastly, they are easily manipulated and can even be arranged to work automatically.

E. F. A.

Inorganic Chemistry.

Purification and Sterilisation of Drinking-water by means of Calcium Peroxide. L. FREYSSINGE and RAUL ROCHÉ (*Rev. intern. Falsif.*, 1905, 18, 49—51).—The addition of about 0.4 gram of calcium peroxide per litre to water completely sterilises the latter. The action is not instantaneous, but in most cases takes about 2 hours. After 3 hours, no living bacteria were found in a water which originally contained 355,000 *Bacilli coli communis* and 171,000 *B. typhosus* per c.c. The peroxide is more rapidly decomposed when a little sodium hydrogen carbonate is added to the water, and the sterilisation is then completed in about 15—20 minutes. The hydrogen peroxide resulting from the decomposition of the calcium peroxide may be removed, together with the precipitate of calcium carbonate, by filtration through manganese dioxide. The hardness of the water is generally diminished by this treatment. If stored in closed bottles, the sterilised but unfiltered water can be kept for a long time before using for drinking.
W. P. S.

Use of Barium Carbonate for the Purification of Water. E. E. BASCH (*Chem. Zeit.*, 1905, 29, 721).—Experiments on a small scale on the softening of water by means of barium carbonate gave good results when an excess of the precipitant was used, and when it was thoroughly mixed with the water.
A. MCK.

Function of the Catalyst in the Deacon Process for the Manufacture of Chlorine. MARIO G. LEVI and V. BETTONI (*Gazzetta*, 1905, 35, i, 320—342).—From experiments on the inter-action of hydrogen chloride and dry air in presence of pumice impregnated with copper salts as catalysts, the authors conclude that the reaction is slowly initiated by the joint action of the high temperature and the pumice and is accelerated by the copper salt, the function of which is to absorb the water formed during the reaction.

An account is given of the different views previously published as to the mechanism of the process.
T. H. P.

Apparatus for the production of Chlorine, Carbon Dioxide, Hydrogen Sulphide, &c. CARL ECKART (*Zeit. anal. Chem.*, 1905, 44, 398—399).—The evolution part of the apparatus consists of a three-necked Woulfe's bottle. The stem of a tapped funnel is ground into the middle neck, a tube leads from one of the other necks to the top of the funnel, and the third neck carries the delivery tube. The latter passes to a wash-bottle containing a little water, from which the gas is led to the bottom of a large flask nearly filled with water and surrounded by a vessel containing ice-water. A side-tube, leading from the top of this flask, passes into a wash-bottle containing water to the height of about 15 cm. By the slight pressure thus produced, a concentrated solution of the gas is obtained in the flask, and scarcely

any of the gas escapes into the room. The gas is produced by allowing hydrochloric acid to fall drop by drop from the tapped funnel on to marble, bleaching powder, &c., contained in the Woulfe's bottle. India-rubber connections and screw-cocks are provided between the various parts of the apparatus.

W. P. S.

Ozonising of Oxygen and Atmospheric Air by the Discharge from Metallic Points. E. WARBURG (*Ann. Physik*, 1905, 17, 1—29).—A continuation of the author's previous paper (Abstr., 1904, ii, 24). The arsenious acid and potassium iodide methods for the estimation of ozone are compared, the latter being considered preferable. The influence of pressure on the ozonisation has been investigated, and the yield per ampere-minute is found to increase with increasing pressure. This the author considers to be due solely to the greater number of molecules encountered by the ions, and not to increase in the ozonising power. At constant pressure, the yield decreases with rise of temperature, but at constant concentration the effect of temperature is slight, a rise from the ordinary temperature to 80° causing a small increase for small currents and a small decrease for higher currents. It has been shown previously that with a negative potential the yield is greatest for very small currents, and it is further found that with increasing current a minimum is reached, after which the yield again rises. With positive potential, the yield increases with the current, so that the potential should be near the sparking point; it increases also with increasing distance between point and plate, but this distance cannot be too great owing to the decreasing current. The ozonisation of atmospheric air has also been investigated: with a negative point the yield is about one-fifth of that obtained with pure oxygen, but with a positive point the value increases to about one-half. The author considers his work further confirms his previous opinion that the ozone production is due to photo- and cathodo-chemical action.

L. M. J.

Reduction of Sulphates. CAMILLO BRÜCKNER (*Monatsh.*, 1905, 26, 675—682).—The author has studied the reduction of anhydrous sulphates by heating with magnesium powder in an atmosphere of nitrogen in a test-tube. If more than one atom of magnesium be mixed with each mol. of sulphate, the reaction increases in violence without any change in the final products. The reduction is accompanied, except in the case of the alkali sulphates, by an evolution of sulphur dioxide, which takes place with explosive violence if more than 0.3 gram of the reaction mixture is heated at once.

The reduction of the alkali sulphates is accompanied by intense luminosity of the mixture; the reaction products, which become red on cooling or green on exposure to air, contain polysulphides and thio-sulphates, and yield alkaline solutions when extracted with water; the products are not altered if the reaction is carried out in an open tube or in a crucible.

The reduction of the sulphates of magnesium, calcium, barium, zinc, aluminium, or nickel by magnesium powder results in the formation of sulphur dioxide, sulphur, magnesium oxide, and the

oxide, sulphide, and thiosulphate of the metal ; owing to the ease with which cupric oxide is reduced, the residue from the reduction of copper sulphate contains also cuprous oxide and copper, whilst manganese and ferric sulphates, which possess strong tendencies to auto-oxidation, yield the higher oxides of the metals along with the sulphides and thiosulphates.

Reduction of these sulphates with formation of the sulphides takes place also when the anhydrous salts are ground with magnesium powder in a mortar.

The formation of the thiosulphate may be due to the action of liberated sulphur on intermediately formed sulphite, or to the interaction of sulphur, magnesium oxide, and sulphur dioxide, as when these are heated together and the product extracted with water the aqueous solution contains the thiosulphate.

As sulphur trioxide appears as an intermediate product in the reduction of some unstable sulphates, it was passed over heated magnesium powder, when sulphur dioxide was evolved, and the residue contained magnesium oxide and sulphide. G. Y.

Selenic Acid. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1905, 150—151).—The sp. gr. of three commercial samples of selenic acid were: No. 1, 1·4669 at 15·5°, No. 2, 1·4386 at 18°, and No. 3, 1·4698 at 15·8°. The sp. gr. of several mixtures of selenic acid and water at different temperatures are tabulated in the original.

T. A. H.

The True Atomic Weight of Nitrogen. GUSTAV D. HINRICHS (*Compt. rend.*, 1905, 140, 1590—1591).—The author draws attention to the fact that the values recently obtained by Guye for the atomic weight of nitrogen (compare Abstr., 1904, ii, 475, 557, 812) closely approach the value 14·00, which he maintains is the true atomic weight of nitrogen (compare Abstr., 1893, ii, 163, 277, 316, 317; 1894, ii, 39, 87, 276; 1900, ii, 534, 539).

M. A. W.

Oxidation of Atmospheric Nitrogen in the High Tension Arc. ALFRED STAVENHAGEN (*Ber.*, 1905, 38, 2171—2177).—Air was forced at known rates through a cooled porcelain tube containing two iron electrodes; the tension was about 20,000 volts and the current 0·07 ampere, the discharge being a continuous greenish-yellow flame. Large quantities of oxides of nitrogen were formed, the yield being a maximum when air was forced through at a velocity of 180 litres per hour. It is impossible to completely condense all the oxides of nitrogen formed in this manner even by means of liquid air.

E. F. A.

Constitution of Frémy's Sulphazilate and Pelouze's Nitrosulphate. EDWARD DIVERS (*Ber.*, 1905, 38, 2252).—A correction (compare this vol., ii, 449).

W. A. D.

Action of Fluorine on Oxygenated Compounds of Nitrogen. HENRI MOISSAN and PAUL LEBEAU (*Compt. rend.*, 1905, 140, 1573—1577).—The authors have examined the behaviour of fluorine

with the oxides of nitrogen, it having been previously observed that it reacts violently with nitric acid (compare Moissan, *Ann. Chim. Phys.*, 1891, [vi], 24, 251). Fluorine has no action on nitrogen peroxide or nitrous oxide at the ordinary temperature.

When a mixture of nitrous oxide and fluorine is heated electrically by means of a platinum spiral, platinum fluoride is formed at 400° , or if the two gases are heated to redness in a glass vessel, silicon fluoride and oxygen are formed, whilst the nitrous oxide remains unaltered. When a mixture of nitrous oxide and fluorine is submitted to the action of an induction spark in the presence of mercury, there is a complex reaction, the mercury is attacked, and the final gaseous mixture contains oxygen, nitrogen, and nitrous oxide, but no compound of nitrogen and fluorine. Fluorine combines with nitric oxide with production of a pale yellow flame, and when the nitric oxide is in excess no volatile compound of fluorine is obtained, but the heat developed by the reaction decomposes the nitric oxide into nitrogen and oxygen, the oxygen reacting with the excess of nitric oxide to form nitrogen peroxide. By the action of nitric oxide on excess of fluorine at the temperature of liquid oxygen, a white solid is obtained, which yields on vaporisation fluorine and a colourless liquid boiling above -80° , and containing nitrogen, fluorine, and oxygen.

M. A. W.

Preparation and Properties of Nitroxyl Fluoride (Nitryl Fluoride). HENRI MOISSAN and PAUL LEBEAU (*Compt. rend.*, 1905, 140, 1621—1626. Compare preceding abstract).—By repeated fractional distillation of the white solid obtained by the action of excess of fluorine on nitric oxide at the temperature of liquid oxygen, all the dissolved fluorine is removed and the residue, which is liquid at -80° , is *nitroxyl fluoride* (*nitryl fluoride*), NO_2F , its preparation from nitric oxide and fluorine being represented by the equation $4\text{NO} + \text{F}_2 = 2\text{NO}_2\text{F} + \text{N}_2$. Nitroxyl fluoride is a colourless gas which attacks the mucous membrane, producing a painful and persistent irritation; it melts at -139° , boils at -63.5° , has a density 2.17—2.31 at 0° , the theoretical value being 2.26; it does not combine with hydrogen, sulphur, or carbon in the cold, but reacts at the ordinary temperature with boron, silicon, phosphorus, arsenic, antimony, iodine, the alkali metals, and the metals of the alkaline earths, thorium, aluminium, iron, or mercury; it decomposes cold water, producing hydrofluoric acid and nitric acid; the reaction is quantitative and has served in the analysis of the compound; it also reacts with a large number of organic compounds, yielding, with benzene, nitrobenzene and a volatile product which attacks the eyes.

M. A. W.

Silicochloroform. OTTO RUFF and KURT ALBERT [and, in part, EMIL GEISEL] (*Ber.*, 1905, 38, 2222—2243).—Silicochloroform is best prepared according to Combe's method by the action of dry hydrogen chloride on commercial 20 per cent. copper silicide; the gaseous product is condensed by passing it through a worm surrounded by a freezing mixture, the receiver being kept in liquid air. The pure substance obtained after very careful fractionation boils at 33° under 758 mm. pressure, melts and solidifies at -134° (air thermometer), and has a sp. gr. 1.3438 at 15° ; from the latter value, the atomic

volume of silicon in silicochloroform is 58.33. Silicochloroform is completely miscible with carbon disulphide, carbon tetrachloride, chloroform, silicon tetrachloride, stannic chloride, titanous chloride, and arsenic trichloride. It decomposes at 800° according to the equation $4\text{SiHCl}_3 \rightleftharpoons \text{Si} + 3\text{SiCl}_4 + 2\text{H}_2$, the action being reversible; it is, however, not attacked at 150° by sodium, sodium amalgam, mercury, copper, tin, sulphur, or aluminium chloride. Chromic anhydride decomposes it at 160° apparently according to the equation $3\text{SiHCl}_3 + 5\text{CrO}_3 = \text{Cr}_2\text{O}_3 + 3\text{SiO}_2 + 3\text{Cr}_2\text{O}_3\text{Cl}_2 + 3\text{HCl}$; with sulphur trioxide at the same temperature, the following action occurs: $2\text{SiHCl}_3 + 4\text{SO}_3 = \text{SO}_2\text{Cl}_2 + \text{HCl} + \text{SiO}_2 + 2\text{SO}_2 + \text{SiOCl}_2 + \text{SO}_3\text{HCl}$. Dry sulphur dioxide leaves a large proportion of the silicochloroform unchanged, but the following action also occurs: $\text{SO}_2 + 2\text{SiHCl}_3 = \text{S} + \text{SiO}_2 + \text{SiCl}_4 + 2\text{HCl}$. With arsenious oxide moistened with sodium hydroxide solution, the action $\text{As}_2\text{O}_3 + 18\text{NaOH} + 3\text{H}_2\text{O} + 6\text{SiHCl}_3 = 18\text{NaCl} + 6\text{Si(OH)}_4 + \text{As}_2$ appears to take place; with antimony oxide, a similar change occurs, antimony being liberated. Arsenic trichloride, stannic chloride, boron trichloride, and titanium tetrachloride are not changed by silicochloroform at 150° , but bring about a catalytic decomposition of the latter, hydrogen being formed.

On passing dry gaseous ammonia mixed with hydrogen into a Woulfe's bottle, cooled at 15° , into which silicochloroform diluted with hydrogen is simultaneously led, a white powder having the composition $\text{N}:\text{SiH}, 3\text{NH}_4\text{Cl}, 0.2\text{NH}_3$ is obtained; the ammonium chloride may be almost completely removed by washing the product with liquefied ammonia in an apparatus from which moisture is excluded; but attempts to remove the ammonia completely, either at the ordinary temperature in a vacuum, or at 100° , cause partial decomposition according to the equation $\text{SiNH} + \text{NH}_3 = \text{Si(NH)}_2 + \text{H}_2$.

Siliconitrogen hydride, SiH:N , is a white powder with a caustic taste, which is decomposed by water or sodium hydroxide solution giving hydrogen, thus: $\text{SiHN} + 4\text{NaOH} = \text{Si(ONa)}_4 + \text{NH}_3 + \text{H}_2$; the action is quantitative. It has all the reducing properties of silicoformic anhydride, and is converted by dry hydrogen chloride at 300° into silicochloroform and ammonium chloride. W. A. D.

New Allotropic Form of Carbon and its Heat of Combustion.

WILLIAM G. MIXTER (*Amer. J. Sci.*, 1905, 19, 434—444).—The heat of combustion of 1 gram of carbon obtained by the decomposition of acetylene is found to be 7894 cals., the corresponding values for sugar charcoal and graphite being respectively 8057 and 7831. The value is hence very different from that for amorphous carbon and approaches that for graphite. Moissan has, however, shown that this carbon is not graphite. It has a sp. gr. 1.919 at the ordinary temperature. It is found that it does not exert the catalytic actions of charcoal, and that it only absorbs 0.1 per cent. of its weight of moisture from the atmosphere. When heated with sulphuric acid, there is no odour of sulphur dioxide. L. M. J.

Mutual Relationships of the Different Modifications of Carbon. RUDOLF SCHENCK and W. HELLER (*Ber.*, 1905, 38, 2139—2143).—Starting with the equation $P = \zeta \cdot 1 + \eta/\eta^2$, where P is the

total gas pressure, ζ is the equilibrium constant for the system C, CO, CO₂, and η the similar constant for the system Fe, FeO, CO, CO₂; since η does not vary with different varieties of carbon, it follows that at constant temperature the value of ζ for the various modifications of carbon is proportional to the total gaseous pressure. The pressures have been determined at temperatures between 400° and 800°, when the various varieties of carbon are in equilibrium with metallic iron, ferrous oxide, and the oxides of carbon. The apparatus employed was the same as for the experiments already described (this vol., ii, 526). The ferrous oxide was obtained by heating dry ferrous oxalate at 300° under reduced pressure in a quartz tube and in the presence of powdered carbon. The mixture was then heated to a higher temperature, when part of the carbon reduced the ferrous oxide, all gases were removed, and the pressure determined when equilibrium was attained. The results show that at the same temperature the highest pressures are given by amorphous carbon and the lowest by graphite. Powdered diamond is intermediate between the two, but the values approximate closely to those of amorphous sugar carbon. The powdered carbon obtained by decomposing carbon monoxide gives values identical with those for graphite. Within the temperature limits examined, the temperature-pressure curves do not cut one another, and within these temperatures graphite is the most stable modification.

It follows that for any given temperature in a blast furnace worked with wood charcoal the composition of the gaseous mixture will be different (richer in carbon monoxide) from the gaseous mixture of a furnace worked with coke (which is allied to graphite).

J. J. S.

State in which Helium exists in Pitchblende. RICHARD J. MOSS (*Sci. Trans. Roy. Dubl. Soc.*, 1904, [ii], 8, 153—160).—Pitchblende was first ground in a vacuum and then decomposed by fusion with potassium hydrogen sulphate. The helium liberated by grinding in a vacuum was 1·17 per cent. of the total quantity present in one specimen, 1·11 per cent. of the total quantity in another specimen. The total quantity of helium obtained per gram of mineral was 0·107 c.c. in the first case, 0·082 c.c. in the second case. The first specimen yielded also in all 4·686 c.c. of carbon dioxide per gram, but of this only 0·0085 per cent. was obtained by grinding in a vacuum. Water vapour is by far the most abundant of the substances liberated by grinding pitchblende in a vacuum.

There is a strong presumption that, although no cavities can be detected in pitchblende by microscopic examination, they nevertheless exist, and it is probable that the helium is contained in such cavities. The most minute subdivision that can be effected by mechanical means would open only a small proportion of these cavities.

J. C. P.

Transformation of Potassium Chlorate into Iodate by Iodine in presence of Nitric Acid. MAX SCHLÖTTER (*Zeit. anorg. Chem.*, 1905, 45, 270—274).—The transformation of potassium chlorate into the iodate by heating with iodine in presence of nitric acid is dependent

(1) on the concentration of the acid. With dilute acid the reaction is : $10\text{KClO}_3 + 6\text{I}_2 = 10\text{KIO}_3 + 2\text{HIO}_3 + 10\text{HCl}$; with more concentrated acid : $2\text{KClO}_3 + \text{I}_2 = 2\text{KIO}_3 + \text{Cl}_2$. (2) On the proportions of iodine to perchlorate. With $\text{KClO}_3 : \text{I}_2 = 2 : 1$ the reaction is : $2\text{KClO}_3 + \text{I}_2 = 2\text{KIO}_3 + \text{Cl}_2$; with $\text{KClO}_3 : \text{I}_2 = 1 : 1$, the reaction is : $\text{KClO}_3 + \text{I}_2 = \text{KIO}_3 + \text{ICl}$.
D. H. J.

Specific Gravities of Sodium Carbonate and Sodium Hydroxide Solutions. RUDOLF WEGSCHEIDER and HEINRICH WALTER (*Monatsh.*, 1905, **26**, 685—725).—Sp. gr. determinations are given for solutions of sodium carbonate and of sodium hydroxide, as well as of mixtures of these at temperatures between 60° and 80° . The sp. gr. of pure solutions of these salts of a strength not greater than $8N$, at temperatures between 0 — 100° or 15 — 80° respectively, are represented by the equation $d_t = d'_w + (a + bt + ct^2)X + (a' + b't + c't^2)X^2$, where d'_w is the sp. gr. of pure water at the given temperature, X is the normality or the percentage composition of the solution, and $a, b, c, a', b',$ and c' are constants. The error is usually under 0.002 . The sp. gr. of mixed solutions of sodium carbonate and hydroxide may be calculated approximately according to the law of mixtures. By applying a small correction which is a linear function of the temperature, formulæ are obtained from which the sp. gr. of either simple or mixed solutions of sodium carbonate and hydroxide, of not more than $8N$ and at temperatures between 10° and 80° , may be calculated with an error of a few units in the third decimal place.
G. Y.

Action of Sodium Polysulphide on Sodium Hyposulphite. ARTHUR BINZ (*Ber.*, 1905, **38**, 2051—2056. Compare Abstr., 1904, i, 964).—When sodium hyposulphite acts on sodium polysulphide in the presence of sodium hydroxide, sulphite and sulphate are formed, whilst thiosulphite is possibly produced as an intermediate product, thus: $\text{Na}_2\text{S}_2\text{O}_4 + \text{Na}_2\text{S}_2 + 2\text{NaOH} = \text{Na}_2\text{S}_2\text{O}_2 + \text{Na}_2\text{SO}_3 + \text{Na}_2\text{S} + \text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_2 + 2\text{NaOH} = \text{Na}_2\text{S} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$. The action of sodium thiosulphate on sodium hyposulphite is analogous to that of sodium polysulphide, but takes place more slowly.
A. McK.

Action of Oxygen on Cæsium-ammonium. ÉTIENNE RENGADE (*Compt. rend.*, 1905, **140**, 1536—1538).—Cæsium-ammonium dissolved in liquid ammonia at -60° rapidly absorbs oxygen, forming the monoxide, Cs_2O_2 , as a pale red, crystalline powder which melts to a yellow liquid and solidifies on cooling to a white, crystalline mass. The oxide, Cs_2O_2 , is obtained in the form of small, deep brown, lozenge-shaped crystals by the direct oxidation of the monoxide suspended in liquid ammonia, and is converted into the peroxide, Cs_2O_4 , by the prolonged action of oxygen in the same medium; the peroxide forms small, yellow needles. When the oxidation of cæsium-ammonium in liquid ammonia is carried out very slowly, the cæsium monoxide reacts with the cæsium-ammonium to form cæsium hydroxide and cæsamide (compare this vol., ii, 388), and if the mixture be heated reaction

occurs between the cæsamide and cæsium oxide with the formation of cæsium and nitrogen according to the equation $\text{Cs}_2\text{O}_2 + \text{CsNH}_2 = 2\text{CsOH} + \text{Cs} + \text{N}$.
M. A. W.

Influence of Silver Nitrate on the Solubility of Silver Nitrite. ALEX. NAUMANN and ADOLF RÜCKER (*Ber.*, 1905, 38, 2292—2295).—The experiments of Nernst (*Abstr.*, 1890, 3) on the influence of sodium acetate on the solubility of silver acetate have been repeated, and that author's results confirmed. Similar results are obtained on adding silver nitrate to a saturated aqueous solution of silver nitrite. At 18°, saturated solution contains 3.1823 grams = 0.02067 mol. of silver nitrite per litre; the following table gives the solubility of silver nitrite per litre in presence of silver nitrate:

Silver nitrate added in mol. per litre.	Silver nitrite remaining in solution.		
	Found.	Calculated.	
		According to van't Hoff.	Allowing for partial dissocia- tion of silver nitrate.
$0.00258 = \frac{1}{4} \times 0.02067$	0.01975	0.01943	0.01946
$0.00517 = \frac{1}{2} \times 0.02067$	0.01900	0.01826	0.01846
$0.01033 = \frac{1}{2} \times 0.02067$	0.01689	0.01615	0.01639
$0.02067 = 1 \times 0.02067$	0.01435	0.01281	0.01335
$0.04134 = 2 \times 0.02067$	0.01168	0.00843	0.00939
$0.08268 = 4 \times 0.02067$	0.00961	0.00490	0.00573

As with sodium and silver acetates, the variation of the experimental from the calculated results increases with the amount of the second salt added (compare also Noyes, *Abstr.*, 1891, 142). G. Y.

Dissociation of the Carbonates of the Alkaline Earths and of Magnesium Carbonate. OTTO BRILL (*Zeit. anorg. Chem.*, 1905, 45, 275—292).—The dissociation temperature, at which the pressure of the dissociation products is equal to one atmosphere, of calcium carbonate is 825°, and of strontium carbonate 1155°. Magnesium carbonate on heating gives a series of basic carbonates with the following formulæ and dissociation temperatures: $10\text{MgO}, 9\text{CO}_2$, 265°; $9\text{MgO}, 8\text{CO}_2$, 295°; $8\text{MgO}, 7\text{CO}_2$, 325°; $7\text{MgO}, 6\text{CO}_2$, 340°; $6\text{MgO}, 5\text{CO}_2$, 380°; $5\text{MgO}, 4\text{CO}_2$, 405°; $7\text{MgO}, \text{CO}_2$, 510°. Calcium, strontium, and barium may be estimated in presence of one another as follows: from 2 to 3 milligrams of the mixed precipitated carbonates (dried at 200°) are weighed in a small platinum crucible (3 mm. high) on a Nernst microbalance and heated by means of a platinum-wire electric furnace for ten minutes, first at 920° and then at 1170°. The losses of weight at these two temperatures will be the weights of CO_2 corresponding

with the calcium and strontium carbonates respectively; the residue will be unchanged barium carbonate. For control, the carbon dioxide corresponding with the barium carbonate may be determined by igniting the residue with a definite weight of borax and ascertaining the loss of weight.

D. H. J.

Monocalcium Silicate. RUDOLF BENZIAN (*Chem. Zeit.*, 1905, 29, 737—738).—Calcium silicate, prepared by heating sand and chalk in a graphite crucible, forms hexagonal crystals, which are decomposed by water slowly at the ordinary temperature and more quickly when boiled. When calcium silicate was left in contact with water and an aqueous solution of calcium hydroxide for several weeks, it was unchanged in crystalline appearance when the crystals examined were dried at 100°. Hydration had, however, taken place, as an examination of the moist crystals showed; these underwent dehydration when dried at 100°.

A. McK.

Magnesium Aluminium Alloys. G. GRUBE (*Zeit. anorg. Chem.*, 1905, 45, 225—237).—A complete fusion diagram has been worked out by the method already described (this vol., ii, 320). The melting point curve consists of four branches, intersecting at the eutectic points corresponding with a temperature of 451.6° ($\pm 1.1^\circ$) and 35 per cent. of magnesium and a temperature of 439.9° ($\pm 1.1^\circ$) and 68 per cent. of magnesium respectively. The second and third branches intersect at a well-defined maximum point at 462.7°, indicating the existence of a compound Al_3Mg_4 ; this compound forms silver-white, very brittle crystals. The alloys of magnesium, used technically under the name magnalium, contain from 5 to 30 per cent. of magnesium; their hardness increases with the percentage of magnesium. The last alloy of this group is seen from the diagram to contain 35 per cent. of magnesium. The alloys on the second branch of the curve form homogeneous conglomerates of mixed crystals which are hard and brittle but are susceptible of a very high polish and may be used for the manufacture of mirrors. Alloys with 55 to 68 per cent. of magnesium consist of crystals of the hard compound Al_3Mg_4 and the soft eutectic mixture. Alloys with 68 to 100 per cent. of magnesium oxidise easily in the air.

D. H. J.

Solubility of Lead Sulphate in Ammonium Acetate Solutions. ARTHUR A. NOYES and WILLIAM H. WHITCOMB (*J. Amer. Chem. Soc.*, 1905, 27, 747—759).—This investigation was undertaken with the object of ascertaining the cause of the solubility of lead sulphate in ammonium acetate solutions.

Determinations of the conductivity at 25° of lead acetate solutions of concentrations between $N/2$ and $N/192$ have shown that lead acetate is much less ionised than are the acetates of barium, manganese, nickel, cobalt, zinc, and cadmium, and that, assuming that lead acetate dissociates into three ions, its degree of ionisation amounts to only about 22 per cent. at a concentration of $N/10$.

Qualitative migration experiments with saturated solutions of lead sulphate in N ammonium acetate solution are described, which lead to

the conclusion that the lead is present in the acetate solution almost entirely in the un-ionised state.

Lead sulphate is soluble to the extent of 0.636 gram per litre in 0.104*N* ammonium acetate solution at 25°, 1.38 grams per litre in 0.207*N*, and 3.06 grams per litre in 0.414*N* solution, the solubility being roughly proportional to the concentration of the ammonium acetate. Rough experiments have shown that lead sulphate has approximately the same solubility in sodium acetate solution as in an ammonium acetate solution of equivalent strength.

From the results of these experiments, it is concluded that the increased solubility of lead sulphate in acetate solutions is due mainly to the formation of un-ionised lead acetate by metathesis.

E. G.

Colloidal Copper Oxide. HEINRICH LEY (*Ber.*, 1905, **38**, 2199—2203).—*Copper succinimide*, $(C_4O_2NH_4)_2Cu \cdot 6H_2O$, obtained by decomposing mercury succinimide suspended in water with copper amalgam, forms blue leaflets or needles and melts and loses water at 160—165°. The conductivity of its aqueous solutions is small, showing that the salt is only slightly dissociated. It is, however, easily hydrolysed; its aqueous solution after a few days changes its colour from blue to dark green and brown. A precipitate of hydroxide or oxide does not, however, separate even after several weeks, but the hydrolysis is shown to be nearly complete by cryoscopic measurements. The succinimide may be removed by dialysis, but the dialysed solutions containing colloidal copper oxide are less stable than when in presence of succinimide. Electrolytes, such as chlorides or nitrates, rapidly cause a separation of gelatinous copper hydroxide from either the original or dialysed solutions.

W. A. D.

Copper-Zinc Alloys. OTTO SACKUR [with P. MAUZ and A. SIEMENS] (*Ber.*, 1905, **38**, 2186—2196).—Curves have been plotted for various properties of all possible alloys of zinc and copper in order to ascertain at which compositions breaks occur denoting the formation of definite compounds. Thus the curve portraying the velocity of precipitation of copper from its salts shows well-marked breaks corresponding with alloys containing 41—45 per cent. and 60—62 per cent. of copper. Similarly, curves giving the rate of dissolution of alloys in acids indicate breaks at the same points. The melting-point curve shows breaks corresponding with 32.6 per cent., 49.5 per cent., and 54.6 per cent. of copper. The first of these corresponds with the alloy $CuZn_2$, the second with $CuZn$, the third with mixed crystals of $CuZn$ and Cu .

The breaks in the curves occur with alloys containing more copper than the simple compounds $CuZn_2$ and $CuZn$ require. It is suggested that a dissociation equilibrium exists in the fused alloy between the compound and its components $Cu_xZn_y \rightleftharpoons xCu + yZn$, and that the free zinc only disappears when copper is present in a certain excess.

E. F. A.

Anhydrous Neodymium Chloride. CAMILLE MATIGNON (*Compt. rend.*, 1905, 140, 1637—1639. Compare Abstr., 1901, ii, 602, and this vol., ii, 391).—Neodymium chloride, unlike samarium chloride, is not attacked by hydrogen even at 1000°. Chlorine, phosphine, and aluminium phosphide have also no action on the salt. Oxygen converts it into *neodymium oxychloride*, NdOCl , which crystallises in brilliant, mauve-tinted lamellæ which have no action on polarised light and probably belong to the cubic system. The oxychloride is infusible at 1000°. Hydrogen iodide, when heated with neodymium chloride, slowly transforms it into the *iodide*, NdI_3 . This is black and fuses to a black liquid, which at a higher temperature suddenly becomes transparent, apparently owing to the formation of an allotropic modification. *Neodymium bromide*, prepared by the action of hydrogen bromide on the chloride at high temperatures, closely resembles the latter in tint and crystalline form, but melts to a dark coloured liquid. Ammonia has no action on neodymium chloride at the atmospheric temperature, but forms additive compounds when heated with it. When acetylene is heated with neodymium chloride, the latter is unattacked, but the acetylene polymerises, and carbon is deposited in a form having a brilliant reflecting surface; this carbon is not graphitic. T. A. H.

Compounds of Aluminium Chloride with Carbonyl Chloride. E. BAUD (*Compt. rend.*, 1905, 140, 1688—1689).—Aluminium chloride dissolves in liquid carbonyl chloride, and on evaporation of the solution at the ordinary temperature a colourless liquid remains which solidifies at -2° and has the composition $2\text{AlCl}_3 \cdot 5\text{COCl}_2$. Its dissociation tension is equal to 760 mm. at 30° . By removal of carbonyl chloride, the compound $2\text{AlCl}_3 \cdot 3\text{COCl}_2$ is formed; this has a dissociation tension of 760 mm. at 55° . On further removal of carbonyl chloride, the compound $4\text{AlCl}_3 \cdot \text{COCl}_2$ is obtained in the form of silky needles which do not decompose to an appreciable extent below 750° . The last two compounds are formed when aluminium chloride is distilled in a current of dry carbonyl chloride, and also when the vapour of aluminium chloride is led by means of a current of carbonic oxide through a red-hot tube. These two compounds are present in commercial aluminium chloride. To purify this, it should be sublimed fractionally in a current of hydrogen or nitrogen. H. M. D.

Preparation of Binary Metallic Compounds by means of Aluminium Powder. A. COLANI (*Compt. rend.*, 1905, 141, 33—35. Compare Matignon, Abstr., 1900, ii, 482, and Fonzes-Diacon, *ibid.*, 405).—An intimate mixture of the oxide of the metal with the non-metallic element or its oxide and finely powdered aluminium is placed in a crucible lined with magnesia and the mixture is inflamed by means of a magnesium cartridge. Where difficultly fusible products are expected, it is advantageous to add to the contents a mixture of cupric oxide or stannic oxide with aluminium powder, as these, when inflamed, produce intense heat.

Sulphides separate with difficulty from the alumina simultaneously formed. Impure specimens of manganese and iron phosphides were obtained, as also specimens of uranium arsenide and antimonide, each

containing some alumina, and of iron silicide and a mixture of iron borides.

T. A. H.

Properties of Tin-Aluminium, Bismuth-Aluminium, and Magnesium-Aluminium Alloys. HECTOR PÉCHEUX (*Compt. rend.*, 1905, 140, 1535—1536).—The gas evolved by the thermochemical action of recently filed alloys of aluminium with tin, bismuth, or magnesium on water (compare Abstr., 1904, ii, 487, 564, 618) consists of hydrogen only, the oxygen of the water oxidising the aluminium; 2 c.c. of the alloy SnAl_3 produce 5—6 c.c. of hydrogen in 20 minutes. A solution of copper sulphate of sp. gr. 1.1 is readily decomposed by the alloys; the alloy SnAl_3 evolves 5 c.c. of hydrogen in 20 minutes, the alloy BiAl three times that quantity, whilst the alloy MgAl causes a very rapid decomposition. The alloys ZnAl or PbAl , which have no action on water, decompose copper sulphate solution and slowly decompose zinc sulphate solution.

M. A. W.

Constitution and Properties of Aluminium Steels. LÉON GUILLET (*Compt. rend.*, 1905, 141, 35—36).—Aluminium has but little influence on the mechanical properties of steel so long as the amount present is less than 2 per cent. Up to 15 per cent., the aluminium dissolves in the iron and this solution does not dissolve carbon. The perlite in these steels is compact and granular (to this is due the brittleness of some specimens) and is not converted into martensite by tempering. When much aluminium is present, free martensite may occur even in steels containing less than 0.85 per cent. of carbon.

T. A. H.

Reactions in the Reduction of Iron. RUDOLF SCHENCK and W. HELLER (*Ber.*, 1905, 38, 2132—2139. Compare Schenck and Zimmermann, Abstr., 1903, ii, 423, and Baur and Glaessner, *ibid.*, 423).—When carbon monoxide is heated with metallic iron, the pressure observed after equilibrium is attained is extremely small and it appears that practically all the gas is removed. This is due to the oxidation of the iron and the deposition of the carbon in the solid form. As pure carbon monoxide cannot oxidise iron, it is assumed that the iron reacts in two distinct ways: (1) catalytically, decomposing the monoxide into carbon and the dioxide, (2) as a reducing agent on the dioxide, producing ferrous oxide and carbon monoxide. These two reactions proceed until equilibrium is established between iron, ferrous oxide, carbon, and the two oxides of carbon.

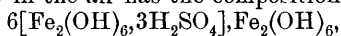
It is shown that the partial pressures of the two oxides of carbon and also the sum of these is dependent on the temperature only or that for each temperature there is a definite partial pressure for each oxide and a definite total pressure. It thus follows that in the blast furnace ferrous oxide will only be reduced by carbon monoxide in the presence of carbon if the total pressure of the monoxide and dioxide is less than the pressure of the total equilibrium. If, on the other hand, the pressure of the gas mixture at the given temperature is greater, then reoxidation of the iron occurs and deposition of carbon.

The pressures for the total equilibrium for temperatures between

400° and 800° have been determined by two methods. (1) Heating carbon monoxide with finely divided iron and measuring the pressure when equilibrium is attained. (2) Heating ferrous oxide and carbon in a vacuum and determining the pressure at fixed temperatures. The two methods give concordant results. Some of the numbers are : 468°, 10.3 mm. ; 620°, 81.5 mm. ; 728°, 438 mm. ; and 780°, 780 mm.

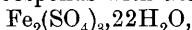
Similar experiments have been conducted with manganese, and as this is much more readily oxidised than iron the pressures are smaller : at 1200°, $P = 10$ mm.; at 1229°, $P = 15.3$. The application of these principles to the metallurgy of iron in the blast furnace is discussed. J. J. S.

Basic Ferric Sulphate. ALBERT RECOURA (*Compt. rend.*, 1905, 140, 1634—1637. Compare Abstr., 1903, ii, 599, 600).—When ferric sulphate is dissolved in its own weight of water and the solution is shaken up with four or five times its volume of acetone and the two liquids are then allowed to remain in contact during two days, the lower aqueous layer gradually solidifies, forming a whitish-brown, voluminous, spongy mass of *basic ferric sulphate*. This is very soluble in water and when allowed to dry in the air has the composition



and when dried at 120°, $6[\text{Fe}_2\text{O}_3, 3\text{H}_2\text{SO}_4], \text{Fe}_2\text{O}_3$. The author considers that the sulphuric acid shown in these formulæ really exists in the salt (compare Wyruboff, Abstr., 1902, ii, 565, 609). T. A. H.

Hydrolysis of Concentrated Solutions of Ferric Sulphate. ALBERT RECOURA (*Compt. rend.*, 1904, 140, 1685—1688).—When the solution obtained by dissolving anhydrous ferric sulphate in its own weight of water, which corresponds with the composition



is left in a closed vessel at the ordinary temperature for several days, a yellowish-white basic salt of the composition $6\text{Fe}_2(\text{SO}_4)_3, \text{Fe}_2\text{O}_3 \text{aq}$ begins to separate after about ten days. The quantity of the deposited salt gradually increases, but separation is not complete until after the expiration of several weeks. A freshly prepared solution begins to deposit the basic salt at once if a little of this is brought in contact with the solution. From a solution corresponding with the composition $\text{Fe}_2(\text{SO}_4)_3, 15\text{H}_2\text{O}$, the basic salt begins to separate at the end of 24 hours, whereas a solution corresponding with $\text{Fe}_2(\text{SO}_4)_3, 28\text{H}_2\text{O}$ can be kept for years without any basic salt being deposited. The deposition is also found to be more rapid at 20° than at 0°. The author supposes that the solutions originally contain basic salt in a soluble form and that the slow deposition is largely conditioned by the gradual transformation of this into a less soluble modification. H. M. D.

Constitution and Properties of Tin, Titanium, and Cobalt Steels. LEON GUILLET (*Compt. rend.*, 1905, 140, 1689—1691).—Steels containing 0.5 per cent. of tin exhibit the same structure as ordinary carbon steels. When the percentage of tin is between 5 and 10, white patches are observed surrounding the perlite. The tin apparently dissolves in the iron and separates in the form of a definite compound. The carbon is always present in the form of carbide and

there is no trace of graphite. A laminated structure is observable if more than 1 per cent. of tin is present, and such steels are extremely hard and brittle. Annealing has the same influence as on ordinary steels, and tempering only gives rise to martensite at those points where perlite previously existed.

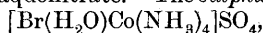
The micrographic examination of steels containing up to 9 per cent. of titanium shows that these have the same structure as ordinary steels and the titanium appears to dissolve in the iron. The mechanical properties are in general but slightly altered, although the breaking weight of steels containing 0.7 per cent. of carbon is considerably increased by the presence of titanium. The effect of annealing and tempering is similar to that on ordinary steels.

Steels containing up to 60 per cent. of cobalt show perlitic structure, and the mechanical properties are only slightly influenced by the cobalt present.

H. M. D.

Bromoquotetra-ammine Cobalt Salts. ALFRED WERNER and A. WOLBERG (*Ber.*, 1905, 38, 2009—2013. Compare this vol., ii, 322).—When $2\text{H}_2\text{O}$ is replaced in hexa-amminecobalt salts by 2NH_3 , diaquotetra-ammine cobalt salts are formed (Jørgensen). The bromo-aquotetra-ammine cobalt salts now described by the authors are intermediate in structure between diaquotetra-ammine salts and dibromotetra-ammine salts, one molecule of water and one atom of bromine being directly attached to the cobalt atom. The relationship between those salts is indicated by the types $[(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_4]\text{Br}_3$, $[\text{Br}(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{Br}_2$, and $[\text{Br}_2\text{Co}(\text{NH}_3)_4]\text{Br}$.

Bromo-aquotetra-ammine cobalt bromide, $[\text{Br}(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{Br}_2$, prepared by warming dibromotetra-ammine cobalt bromide with water and a little hydrobromic acid, forms brownish-violet prisms, the solution of which in cold water is violet and in warm water pink. The corresponding *chloride* forms violet prisms, the solution of which in water is violet. It crystallises with $\frac{1}{2}\text{H}_2\text{O}$. The *nitrate*, $[\text{Br}(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{NO}_3$, prepared by digesting the bromide with a mixture of nitric acid and water, forms reddish-violet crystals; in aqueous solution, it is quickly transformed into the diaquonitrate. The *sulphate*,



separates as violet crystals from a solution of dibromotetra-ammine cobalt sulphate in warm water on the addition of a mixture of alcohol and ether. It may also be prepared by the addition of a mixture of sulphuric acid and alcohol to an aqueous solution of the bromo-aquotetra-ammine bromide.

A. MCK.

Alloys of Nickel and of Cobalt with Iron. W. GUERTLER and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, 45, 205—224).—The freezing point curves for both nickel and cobalt steels and the curves of magnetic transformation for cobalt steels have been determined and complete equilibrium diagrams constructed. The cobalt and nickel steels have also been examined microscopically. A *résumé* of the properties of the alloys of the iron group is given.

The freezing point curve of nickel-iron alloys consists of two branches, of which one, extending from 100 to 35 per cent. of nickel,

exhibits a well-marked minimum. The freezing point curve of cobalt-iron mixtures also consists of two branches, of which one, extending from 100 to 5 per cent. of cobalt, is at the same level as the melting point of cobalt; an addition of iron has no appreciable influence on the melting point of cobalt. During the crystallisation of all these alloys, the crystals have the same composition as the mother liquor.

The mixed crystals of Co—Ni, Co—Fe, and Ni—Fe, which separate from fused masses, are non-magnetic. On cooling, they are transformed into other magnetic varieties of crystals. The curves which express the dependence of the transformation temperature on the composition of the mixed crystals are discontinuous except in the case of the Co—Ni crystals; on the transformation curve for the Ni—Fe crystals there is one break, and on the curve for the Co—Fe crystals three breaks. Hence nickel and cobalt must be considered as isomorphous at temperatures both above and below the transformation curves; two series (magnetic and non-magnetic) of nickel-iron mixtures exist, namely, from 100 to 35 per cent. and from 35 to 0 per cent. of nickel. Two series of non-magnetic Co—Fe crystals and four series of magnetic crystals may be prepared. During the transformation of non-magnetic mixed crystals there does not appear to be any change in the composition of the crystals, except in the case of cobalt-iron crystals containing 80 to 60 per cent. of cobalt. D. H. J.

Constitution of Complex Salts. I. Derivatives of the Sesquioxides. ALEXANDER T. CAMERON (*Proc. Roy. Soc. Edin.*, 1905, 25, 722—737).—The formulæ assigned to the chromoxalates by previous investigators is discussed. It has been stated by Werner (*Trans.*, 1887, 51, 383; 1888, 53, 404) that definite compounds exist corresponding with the formulæ $K_5NH_4Cr_2(C_2O_4)_6 \cdot 6H_2O$ and $KNH_4Cr_2(C_2O_4)_4 \cdot 10H_2O$, and on this ground doubled formulæ were assigned by him to the alkali chromoxalates.

In order to determine whether the blue complex salt corresponding with the first type is a definite compound or an isomorphous mixture of the potassium and ammonium salts, the author prepared a series of blue chromoxalates by crystallisation of solutions containing potassium dichromate, potassium and ammonium hydrogen oxalates, and oxalic acid in different proportions. The percentage of ammonia and the sp. gr. of the crystals was determined. On plotting the specific volume against the percentage of ammonia, a straight line is obtained, which result supports the view that the potassium ammonium chromoxalates are isomorphous mixtures. For some unexplained reason, the specific volume of the pure potassium salt does not fall on the straight line passing through the specific volumes of the mixtures.

In the second part of the paper, the constitution of complex salts of dibasic acids of the type H_2X and of metals forming oxides of the type M_2O_3 is considered. The complex chromoxalates are taken as examples, these being regarded as derivatives of chromic hydroxide in which the hydroxyl groups are substituted by half-saturated oxalate groups. Three chief types, *A*, *B*, and *C*, are distinguished according as three, two, or one hydroxyl group is replaced.

A1, $\text{Cr}(\text{C}_2\text{O}_4\text{K})_3$; A2, $\text{C}_2\text{O}_4[\text{Cr}(\text{C}_2\text{O}_4\text{K})_2]_2$;
 B1, $\text{OH}\cdot\text{Cr}(\text{C}_2\text{O}_4\text{K})_2$, or by loss of water $\text{O}[\text{Cr}(\text{C}_2\text{O}_4\text{K})_2]_2$;
 B2, $\text{HO}\cdot\text{Cr}(\text{C}_2\text{O}_4\text{K})\cdot\text{C}_2\text{O}_4\text{H}$, or by loss of water $\text{C}_2\text{O}_4\cdot\text{Cr}\cdot\text{C}_2\text{O}_4\text{K}$;
 B3, $\text{C}_2\text{O}_4[\text{Cr}(\text{OH})\cdot\text{C}_2\text{O}_4\text{K}]_2$;
 C, $\text{Cr}(\text{OH})_2\cdot\text{C}_2\text{O}_4\text{K}$, or by loss of water $\text{O}\cdot\text{Cr}\cdot\text{C}_2\text{O}_4\text{K}$.

The types A2 and B3 result by elimination of one molecule of potassium oxalate from two molecules of A1 and B1 respectively.

The author shows that nearly all the complex derivatives of the sesquioxides can be referred to one or other of these types, and that monobasic acids can replace the dibasic acids without alteration of the type. A table is given in which the complex compounds yielded by the sesquioxide-forming elements, vanadium, chromium, manganese, iron, cobalt, aluminium, thallium, arsenic, antimony, and bismuth, with hydrochloric, hydrofluoric, hydrocyanic, thiocyanic, nitrous, sulphuric, oxalic, and tartaric acids, are represented according to the above types.

In a similar manner, it is shown that the complex chlorides, fluorides, sulphates, and oxalates of the quadrivalent metals tin, thorium, titanium, and uranium can be represented as derived from the metallic hydroxides according to types in which four, three, and two hydroxyl groups respectively are substituted.

Certain compounds cannot be represented according to the types enumerated. Such are the aluminium oxalates prepared by Rosenheim and Cohn (Abstr., 1896, i, 278), which correspond with the formula $\text{OH}\cdot\text{Al}_2(\text{C}_2\text{O}_4\text{M})_5$, and the amorphous sulphochromosulphates of Recoura (Abstr., 1899, ii, 226).

H. M. D.

So-called Solid Solutions of Indifferent Gases in Uranium Oxides. CARL FRIEDHEIM (*Ber.*, 1905, 38, 2352—2359. Compare Kohlschütter and Vogdt, this vol., ii, 394).—It is suggested that the product obtained by heating hydroxylamine uranate at 125° is not a solid solution of nitrogen and nitrous oxide in uranic acid, but that the decomposition proceeds as follows:

$$\text{UO}_2(\text{O}\cdot\text{NH}_3\cdot\text{OH})_2 \rightarrow \text{UO}_2 \left\langle \begin{smallmatrix} \text{O}\cdot\text{NH}_3 \\ \text{O}\cdot\text{NH}_3 \end{smallmatrix} \right\rangle \text{O}.$$
 Hydroxylamine uranate is known to behave as an acid, and the compound obtained by the action of heat may be regarded as an anhydride, so that the residue after heating consists of this anhydride mixed with a certain amount of uranic acid. The action of acids (H_2SO_4) on the anhydride is to yield uranyl sulphate and $(\text{HO}\cdot\text{NH}_3)_2\text{O}$. This latter loses water, yielding the anhydride of hydroxylamine, $(\text{NH}_2)_2\text{O}$, which immediately decomposes into nitrogen, nitrous oxide, ammonia, hydrogen, and water. Kohlschütter and Vogdt state that hydrogen is not evolved; it is probably used up in reducing the uranium trioxide. The amounts of nitrogen, nitrous oxide, and ammonia agree roughly with those required by above reactions.

J. J. S.

Lithium Uranyl Sulphate and Magnesium Uranyl Sulphate. WILLIAM OECHSNER DE CONINCK and CHAUVENET (*Bull. Acad. roy. Belg.*, 1905, 151—152, 182).—*Lithium uranyl sulphate*, prepared by crystallisation from aqueous solutions containing molecular proportions of the two sulphates, has the formula $\text{Li}_2\text{SO}_4\cdot\text{UO}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$, and closely

resembles the analogous salts already described (this vol., ii, 254, 394, 398).

By an analogous method, a *magnesium uranyl sulphate* of the formula $\text{MgSO}_4 \cdot \text{UO}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ was prepared. T. A. H.

Zirconium Sulphates. OTTO HAUSER (*Zeit. anorg. Chem.*, 1905, 45, 185—204).—Normal anhydrous zirconium sulphate, $\text{Zr}(\text{SO}_4)_2$, is dissolved in large quantity by water; the solution is accompanied by great development of heat, due chiefly to the formation of the hydrated salt, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Sufficiently concentrated solutions can be preserved unchanged, but at a certain degree of dilution there is a separation of the basic salt, $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 14\text{H}_2\text{O}$. The dilution required to produce precipitation of the basic salt increases with rising temperature. The velocity of the reaction is very small, and diminishes rapidly with fall of temperature. Temperatures in the neighbourhood of 40° are best suited to the study of the reaction.

D. H. J.

Preparation and Properties of Thorium Chloride and Bromide. HENRI MOISSAN and MARTINSEN (*Compt. rend.*, 1905, 140, 1510—1515. Compare Berzelius, *Ann. Phys. Chem.*, 1829, 16, 385; Chydenius, *Annalen*, 1863, 127, 33; Troost, *Abstr.*, 1885, 1113; Krüss and Nilson, *Abstr.*, 1887, 704; Moissan and Étard, *Abstr.*, 1896, ii, 422; Matignon and Delépine, *Abstr.*, 1902, ii, 106).—The authors have prepared thorium chloride, ThCl_4 , in the form of colourless crystals by the action of chlorine on thorium carbide at a high temperature, but although the reaction was conducted in a special apparatus free from air and moisture, the product contained traces of the oxychloride due to the action of the thorium chloride on the porcelain tubes. Thorium chloride is only feebly radioactive, dissolves readily in water, and from the saturated solution crystals of the hydrate, $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$, are obtained (compare Cleve, *Abstr.*, 1874, 234); it is soluble also in alcohol or aqueous ether, but insoluble in benzene, toluene, turpentine, chloroform, or carbon disulphide, has a sp. gr. 4.59, sublimates at $720\text{--}750^\circ$, and melts at 820° . Thorium chloride is readily decomposed by fluorine, yields the oxide when heated to redness in a current of oxygen, a mixture of the sulphide and oxysulphide when heated in a current of sulphur vapour and hydrogen, the selenide and phosphide being similarly obtained. By the action of liquid ammonia (Matthews, *Abstr.*, 1890, 295), it is converted into a sparingly soluble ammoniacal thorium chloride. Thorium bromide (Troost and Ouvrard, *Ann. chim. phys.*, 1889, [vi], 17, 227), prepared in the form of transparent crystals by the action of bromine vapour on the flux obtained by fusing a mixture of thoria and carbon in the electric furnace, is unstable in the light, has a sp. gr. 5.62, that of the fused salt being 5.67, sublimates at 710° , and boils at 725° ; it dissolves in water to form the hydrate, $\text{ThBr}_4 \cdot 8\text{H}_2\text{O}$, from which the oxybromide, ThOBr_2 , is obtained by boiling with water in the presence of air, and subsequently drying at 160° ; it behaves similarly to the chloride towards oxygen, sulphur, selenium, phosphorus, or liquid ammonia.

M. A. W.

So-called Explosive Antimony. III. ERNST COHEN and TH. STRENGERS (*Zeit. physikal. Chem.*, 1905, 52, 129—170. Compare Abstr., 1904, ii, 345; this vol., ii, 170).—The authors have determined the heat produced by acting on a known weight of (1) ordinary antimony, (2) non-explosive electrolytic antimony, (3) explosive antimony, or (4) exploded antimony, with a carbon disulphide solution of bromine. The results show that explosive antimony is to be regarded as a solid solution of antimony trichloride, tribromide, or tri-iodide in a metastable form of the metal, referred to as α -antimony. The explosion is the transformation of this α -antimony into ordinary antimony, and the heat of transformation amounts to about 20 cal. per gram. Exploded antimony and non-explosive electrolytic antimony are simply solid solutions of the trichloride, tribromide, or tri-iodide in ordinary antimony. The α -antimony is to be regarded as a monotropic form, for it has been observed that a solution which ordinarily deposits explosive antimony on electrolysis will deposit the stable form if the latter acts as cathode in the solution.

The foregoing interpretation furnishes an adequate explanation of the observations of earlier workers. J. C. P.

Gold in Sea Water. P. DE WILDE (*Arch. Sci. phys. nat.*, 1905, [iv], 19, 559—580).—The presence of gold in sea water, observed from time to time by various authors (for example, M. E. Sonstadt, *Chem. News*, 1872, 26, 159, and A. Liversidge, *J. Roy. Soc. New South Wales*, 1895, 29, 335; also *J. Soc. Chem. Ind.*, 1897, 242), is attributed to the denudation of auriferous rocks, the gold in a very fine state of division being carried by the rivers down to the sea, where it goes into solution probably as bromide or iodide. After describing the methods employed by Sonstadt and Liversidge for the extraction of gold from sea water, the author gives an account of his own process (Belgian Patent No. 156,558), which consists in treating one ton of sea water with 4 or 5 c.c. of a concentrated acid solution of stannous chloride, whereby the gold is converted into "Purple of Cassius." On the addition of half a kilo. of slaked lime, any excess of tin as well as the magnesium salts present in the water are precipitated as hydroxides, and in sinking to the bottom of the vessel carry with them all the purple of Cassius. The gold may be obtained from these hydroxides by extraction with very dilute potassium cyanide ($\frac{1}{2}$ per mil.), and then treating the solution so obtained by one of the known methods, such as metallic zinc, &c. Sea water from the Channel and Mediterranean treated in this way was found to contain no gold, whereas water from the Atlantic and from the mother liquors of the Salin de Rassuen, near Marseilles, yielded traces of that metal. P. H.

Alloys of Gold and Nickel. M. LEVIN (*Zeit. anorg. Chem.*, 1905, 45, 238—242).—By Tammann's methods, a fusion diagram has been worked out for gold-nickel alloys; it gives no evidence of the existence of a definite compound. The cooling curves of alloys containing from 5—20 per cent. and from 50—70 per cent. of nickel show clearly the existence of a crystallisation interval, and with alloys containing 40 per cent. of nickel there is a eutectic horizon at a temperature of 950°.

The fact that the eutectic horizon is well marked only with alloys containing 40 per cent. of nickel, whilst the cooling curves of other alloys of the series show only a "break" at the same temperature, makes it probable that we have to do with the solidification of two series of mixed crystals rather than with a simple eutectic crystallisation of the pure metals. This is confirmed by the microscopic examination of the alloys. Alloys with from 20—90 per cent. of nickel show clearly two contiguous structural elements, of which one is easily, the other slowly, attacked by nitric acid. Alloys with from 5—10 per cent. of nickel are mostly homogeneous.

The transformation point of the nickel-gold alloys lies very near the transformation temperature (323°) of pure nickel, that is, the transformation temperature of nickel is independent of the percentage of gold alloyed with the nickel.

D. H. J.

Colloidal Metals of the Platinum Series. II. ALEXANDER GUTHRIE and GUSTAV HOFMEIER (*J. pr. Chem.*, 1905, [ii], 71, 452—458. Compare this vol., ii, 396).—Colloidal rhodium can be prepared only from pure rhodium salts, as the presence of even traces of impurity prevents the formation of the hydrosol. An unstable liquid hydrosol is formed by reducing rhodium chloride in dilute solution (1 : 1000 aq.) by addition of a few drops of a very dilute solution of hydrazine hydrate (1 : 2000 aq.). In the presence of 1 per cent. of gum arabic the hydrosol is stable, can be concentrated to a certain extent over the water-bath, and on evaporation over sulphuric acid in a vacuum yields the dark brown, solid hydrosol, which contains 99.4 per cent. of rhodium and is almost completely soluble in warm water.

A stable liquid hydrosol of ruthenium hydroxide is obtained by reduction of the double salt, $\text{Ru}_2\text{Cl}_6 \cdot 4\text{KCl}$, by hydrazine hydrate in presence of gum arabic, whilst reduction of potassium ruthenate leads to the formation of a mixed liquid hydrosol of ruthenium and ruthenium hydroxide. The precipitate obtained from this on addition of ammonium chloride contained in one case 89.92 and in another 99.84 per cent. of ruthenium.

The liquid hydrosol of osmium, obtained by reduction of potassium osmate by hydrazine hydrate in gum arabic solution, cannot be obtained free from oxygen (compare Paal and Amberger, *Abstr.*, 1904, ii, 180); on warming with a few drops of concentrated hydrochloric acid, a metallic precipitation is obtained, but the mother liquor contains osmium chloride; the precipitate obtained on addition of ammonium chloride contained 95.44 per cent. of osmium. The solid hydrosol of osmium, obtained by evaporation over the water-bath and finally over sulphuric acid in a vacuum, is almost completely soluble in warm water.

The liquid hydrosols of rhodium, ruthenium, and osmium are decomposed when shaken with barium sulphate or with animal charcoal.

G. Y.

Rendering Active of Hydrogen by Colloidal Palladium. CARL PAAL and CONRAD AMBERGER (*Ber.*, 1905, 38, 2414).—In the

previous experiments (this vol., ii, 397), the hydrogen was passed through the aqueous alcoholic solution of nitrobenzene for three hours.

J. J. S.

Halogen Derivatives of Palladium. ALEXANDER GUTHIER and A. KRELL (*Ber.*, 1905, **38**, 2385—2389. Compare Wilm, *Abstr.*, 1880, 854; Kane, *Phil. Trans.*, 1842, i, 276).—Ammonium palladichloride has the formula $(\text{NH}_4)_2\text{PdCl}_6$. The following new compounds have been prepared: *ammonium palladochloride*, $(\text{NH}_4)_2\text{PdCl}_4$, yellowish-green needles dissolving in water to a dark red solution; *cæsium palladochloride*, pale brown needles; *cæsium palladichloride*, Cs_2PdCl_6 ; *rubidium palladochloride*, Rb_2PdCl_4 ; *rubidium palladichloride*, Rb_2PdCl_6 ; *ammonium palladobromide*, reddish-brown needles; *ammonium palladibromide*, black octahedra; *cæsium palladobromide*, reddish-brown needles; *cæsium palladibromide*, black octahedra; *rubidium palladobromide*, brownish-red needles; *rubidium palladibromide* and *potassium palladibromide*, black octahedra.

The palladous compounds crystallise from aqueous solutions, and on treatment with bromine vapour give the palladic compounds, which are sparingly soluble. All the compounds when carefully heated in a current of hydrogen yield metallic palladium.

J. J. S.

Compounds of Ruthenium with Oxygen. ALEXANDER GUTHIER and F. RANSOHOFF (*Zeit. anorg. Chem.*, 1905, **45**, 243—261).—The tetroxide, RuO_4 , is easily obtained, but efforts to obtain by Claus' method ruthenium monoxide, RuO , or his sesquioxide, Ru_2O_3 , in a pure condition failed, as did likewise attempts to prepare Joly's hydroxide, $\text{Ru}(\text{OH})_4 \cdot 3\text{H}_2\text{O}$, and Debray and Joly's oxides, Ru_2O_5 and Ru_4O_9 . Finely divided ruthenium when heated in the air takes up about 27 per cent. of oxygen and yields apparently a mixture of ruthenium dioxide and ruthenium. By adding potassium hydroxide to a solution of ruthenium sesquichloride, ruthenium sesquihydroxide, $\text{Ru}_2(\text{OH})_6$, is thrown down as a finely divided, dark brown, amorphous precipitate which can be dried over sulphuric acid, and when heated gives ruthenium sesquioxide, Ru_2O_3 , as an intermediate product. The precipitate formed by neutralising an alkali ruthenate with nitric acid is neither pure $\text{Ru}_2(\text{OH})_6$, as assumed by Claus, nor $\text{Ru}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, as assumed by Debray and Joly, but a mixture of ruthenium sesquihydroxide with another anhydrous oxide. A mixed product is also obtained by reducing an alkali ruthenate with alcohol. Ruthenium dioxide, RuO_2 , sublimes in small quantity on heating ruthenium in a stream of oxygen and is obtained quantitatively in the form of blue plates easily reducible by hydrogen by igniting ruthenium sulphate till the weight is constant.

D. H. J.

Mineralogical Chemistry.

The Natural Iron-nickel Alloy, Awaruite. GEORGE S. JAMIESON (*Amer. J. Sci.*, 1905, [iv], 19, 413—415).—Thin sections of water-worn pebbles of "josephinite," from Josephine Co., Oregon, showed that the alloy is of a spongy nature, binding together and enclosing particles of serpentine. Deducting 24.15 per cent. of insoluble silicate, the composition of the alloy is given under I. Analysis II is of a similar alloy from Smith River, Del Norte Co., California; this is a metallic sand with the grains of very uniform size (0.15 mm. diam.), obtained from gold-washings; mixed with it are magnetite and a very little chromite (9.45 per cent. deducted from the analysis).

	Fe.	Ni.	Co.	Cu.	P.	S.	Sp. gr.
I.	25.24	74.17	0.46	—	0.04	0.09	—
II.	21.45	76.60	1.19	0.66	0.04	0.06	7.85
III.	31.02	67.63	0.70	nil	("Awaruite," New Zealand; W. Skey, 1885.)		
IV.	26.60	75.20		nil	(Piedmont; A. Sella, 1891.)		
V.	27.41	71.35	0.65	0.59	("Josephinite," Oregon; W. H. Melville, 1892.)		
VI.	22.30	76.48	nil	1.22	("Souesite," British Columbia; G. C. Hoffman, this vol., ii, 328.)		

Previous analyses of terrestrial iron-nickel alloys are quoted above under III—VI; these are seen to have a certain uniformity in composition, though there seems to be no definite compound of iron and nickel (FeNi_3 corresponds with Fe 24.0, Ni 76.0, and FeNi_2 with Fe 32.2, Ni 67.8 per cent.). The use of several distinct names is thus superfluous, and it is suggested that the earliest name, awaruite, should alone be used. The occurrence of the alloy with serpentine and chromite suggests that it has separated from a basic peridotite magma, and the fact that it is found as a heavy constituent in river sands shows that it is little liable to alteration by oxidation.

L. J. S.

Presence of Chromium and Vanadium in Coal from Liège. ARMAND JORISSEN (*Bull. Acad. roy. Belg.*, 1905, 178—181).—In addition to the elements already observed in the soot produced by the combustion of coal from the deposits in the neighbourhood of Liège (*Abstr.*, 1897, ii, 265, and 1903, ii, 149), the author has now found chromium and vanadium. These elements also occur in the shales associated with this coal, and may be detected by the same methods in the red ash left on complete combustion of these. T. A. H.

Minerals [Tengerite? &c.] from Llano County, Texas. WILLIAM E. HIDDEN (*Amer. J. Sci.*, 1905, [iv], 19, 425—433).—The quarry at the noted gadolinite locality on "Barringer Hill," in Llano Co., has recently been opened up again for the purpose of obtaining a supply of minerals rich in yttrium and erbium, which are used in the construction of the Nernst lamp. Masses of gadolinite

and allanite of over 300 pounds weight and an eighteen-pound mass of yttrialite were found, also enormous crystals, over four feet across, of quartz, felspar, and mica. Other minerals containing rare elements found at the locality include nivenite, mackintoshite, thoro-gummite, fergusonite, cyrtolite, and rowlandite; a preliminary account of the radioactive properties of these is given. A white mineral occurring in small amount as semiglobular or flattened concretions in cracks and fissures in the gadolinite was analysed by W. F. Hillebrand with the following results, from which it appears that the substance may be tengerite, or possibly tengerite mixed with a new beryllium mineral; the occurrence of beryllium as carbonate is new.

Y ₂ O ₃ group (mol. wt.	Ce ₂ O ₃ group (mol. wt.				H ₂ O (>105°).	H ₂ O (<105°).	SiO ₂ .	MgO, Alk. loss.	Total.
226).	335).	Fe ₂ O ₃ .	BeO.	CO ₂ .					
40.8	7.0	4.0	9.7	19.6	14.1	3.2	0.4	1.2	100.0

L. J. S.

Occurrence of Redonda Phosphate in Martinique. ALFRED LACROIX (*Chem. Centr.*, 1905, i, 1613; from *Bull. Soc. franç. Min.*, **28**, 13—16).—The andesite conglomerate which occurs in the island of La Perle, on the N.E. coast of Martinique, is covered with a crust of brown phosphate, which is in places 7 to 8 cm. thick. The zonal structure of the andesite still remains, but the magnetite has completely disappeared. Analysis of the phosphate by Arsandaux gave:

Al ₂ O ₃ , Fe ₂ O ₃ .	CaO.	MgO.	P ₂ O ₅ .	H ₂ O.
34.20	trace	trace	41.20	24.50

The formation of the same phosphate from different minerals is remarkable. In Martinique, it is a decomposition product of hypersthene-andesite; at Chipperton, a product of trachyte; at Connétable, of gneiss and diabase; and at Redonda, of corallite. E. W. W.

Janosite, a New Hydrated Normal Ferric Sulphate. HUGO BÖCKH and KOLMAN EMSZT (*Földtani Közlöny, Budapest*, 1905, **35**, 76—78, 139—142).—The new mineral occurs as a greenish-yellow, powdery efflorescence on graphitic schist in the iron mine at Vashegy, Comitát Gömör, Hungary, where it has resulted by the decomposition of iron-pyrites. Under the microscope, it is seen to consist of minute, orthorhombic plates, which have a perfect basal cleavage and distinct prismatic cleavages; the acute negative bisectrix is normal to the basal plane, and the crystals are markedly pleochroic. Hardness, 2—2½; sp. gr. 2.510—2.548. The substance is soluble in water. The following analysis agrees with the formula Fe₂(SO₄)₃.9H₂O:

Fe.	Al.	SO ₄ .	H ₂ O (250°).	Total.	H ₂ O (100°).	H ₂ O (150°).
20.653	trace	50.715	28.503	99.871	13.519	20.081

The new mineral is thus dimorphous with the rhombohedral coquimbite; it is also near to quenstedtite, [Fe₂(SO₄)₃.10H₂O], in composition, but differs from this in specific gravity, colour, &c. L. J. S.

Epidote from Inverness-shire. HERBERT HENRY THOMAS (*Min. Mag.*, 1905, 14, 109—114).—A band composed largely of epidote, together with garnet, quartz, and actinolite, occurs in gneiss near Barrisdale. The crystals of epidote are dark grey to greyish-brown in colour, and measure up to six inches in length. Complete crystallographic and optical determinations were made, together with the following analysis by W. Pollard :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	H ₂ O.	Total.*	Sp. gr.
39·02	28·64	6·81	0·34	23·73	1·76	100·30	3·37

* Also traces of TiO₂, MnO, MgO.

In its low percentage of ferric iron, this epidote closely resembles that from Huntington, in Massachusetts, described by E. H. Forbes (*Abstr.*, 1896, ii, 371); and, as there pointed out, the refractive indices of the mineral vary with the amount of ferric iron, as shown in the following table :

	Fe ₂ O ₃ .	α .	β .	γ .	$\gamma - \alpha$.	2V over α .
Untersulzbachthal	14·0	1·7305	1·7540	1·7677	0·0372	73°39'
Zillerthal	6·97	1·720	1·7245	1·7344	0·0144	87 46
Inverness-shire ...	6·81	1·714	1·7196	1·725	0·011	89 35
Huntington	5·67	1·714	1·716	1·724	0·010	90 32

L. J. S.

Occurrence of Tantalum and Niobium. JOHANNES SCHILLING (*Zeit. angew. Chem.*, 1905, 18, 883—901).—All analyses previously published of minerals containing tantalum have been collected. The sp. gr. percentage of tantalum and niobium, the localities in which the minerals occur, and references to the literature are tabulated. According to the author, large deposits of tantalum minerals are widely distributed, and as regards the extent of its occurrence in nature, there is nothing to prevent the commercial application of the metal.

H. M. D.

Meteorites of Hvittis and Marjalahti. LEONARD H. BORGSTROM (*Chem. Centr.*, 1905, i, 1667; from *Bull. Com. Géol. Finlande*, 1903, No. 14, 1—80).—*Hvittis*.—This meteoric stone was observed to fall at Hvittis, in Finland, on October 21, 1901; it weighed 14·05 kilos., and buried itself 50—60 cm. in the ground. The mineralogical composition is calculated from analysis I as: enstatite, 59·01; oligoclase, 9·86; nickel-iron, 21·50; oldhamite, 0·86; daubreelite, 0·57; troilite, 7·31; nickel-iron phosphide, 0·50; chromite, 0·32. The enstatite has the composition given under II; the oligoclase (Ab₄An) gave III. Graphite, glass, and an undetermined mineral are also present in small amounts. Under the microscope, the stone is seen to consist of a ground mass of crystallised silicates, embedded in which are irregularly bounded masses of sulphides and metals, as well as a few chondrules.

Marjalahti.—This was seen to fall at Marjalahti, in Finland, on June 1, 1902. The total weight is 44·8 kilos., and the largest mass weighs 22·7 kilos. It belongs to the pallasite type, consisting mainly of nickel-iron and olivine, together with a little troilite and

schreibersite. The nickel-iron contains : Fe, 92.28 ; Ni, 7.13 ; Co, 0.42 per cent. The olivine, which forms about 20 per cent. of the mass, has the composition given under IV ; the non-magnetic troilite contains : Fe, 63.6 ; S, 36.4 per cent. The composition of the schreibersite is given under V. It is pointed out that the phosphide, Fe_2NiP , is of the most frequent occurrence, although there may be isomorphous mixtures of Fe_3P and Ni_3P , with small amount of Co_3P .

	SiO_2 .	Fe.	FeO .	Ni.	Co	Al_2O_3 .	Cr_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	P.	Sp. gr.
I.	41.53	24.66	0.34	1.96	0.07	1.55	0.57	1.41	23.23	0.32	1.26	0.08*	—
II.	59.05	—	0.90	—	—	1.09	—	0.98	37.10	0.47	0.68	—	3.217
III.	63.5	—	—	—	—	22.2	—	4.0	—	1.1	9.2	—	2.60—2.65
IV.	40.26	—	11.86	—	—	—	0.12	—	47.26	0.05	0.21	—	3.38
V.	—	55.15	—	29.15	0.21	—	—	—	—	—	—	14.93	7.278

* Also S, 3.30.

Separation of Iron from Nickel and Cobalt by means of Formic Acid.
—This separation is necessary in every meteorite analysis, but there is no really good method. Ammonium formate solution is prepared by adding ammonia to formic acid solution until it is neutral or only slightly acid. This is added to the neutralised iron solution and the mixture quickly brought up to boiling ; it is then transferred to a dish with hot water and kept up to the boiling point ; in a few minutes the precipitation is complete ; the precipitate is washed with hot water and is then filtered, the filtration taking place much more readily than in other methods. In the first precipitation, the iron precipitate contains only 4.35 per cent. of the nickel and cobalt, and in the second it is quite free from these elements.
L. J. S.

Italian Terrestrial Emanations. II. Gases from Vesuvius, the Flegrei Plains, the Albule Waters of Tivoli, and the Springs of Viterbo, Pergine, and Salsomaggiore. RAFFAELLO NASINI, FRANCESCO ANDERLINI, and ROBERTO SALVADORI (*Memor. R. Accad. Lincei*, 1904, [v], 5, 25—82. Compare Abstr., 1896, ii, 366 ; 1898, ii, 527 ; 1899, ii, 482 ; 1900, ii, 415).—The authors give an account of their chemical and spectroscopical investigations of these various gases and describe the apparatus employed, which comprises mercury pumps automatically charging the gases into Geissler tubes, a pump for extracting and transporting the gas, arrangements for absorbing the nitrogen and burning the hydrocarbons present in the gas, and a device for distilling mercury in a vacuum. Photographs of the various spectra are given and diagrams of the different pieces of apparatus.
T. H. P.

Physiological Chemistry.

Normal Alveolar Carbon Dioxide Pressure in Man. MABEL PUREFOY FITZGERALD and JOHN S. HALDANE (*J. Physiol.*, 1905, 32, 486—494. Compare Haldane and Priestley, this vol., ii, 400).—It was shown previously that whilst the normal alveolar pressure of carbon dioxide remained constant in the same person, it varied in the two individuals experimented on. It being of interest to ascertain the limits in different people, a large number of observations were made, and the results are given in tables. These are then classified and averages given for men, women, boys, and girls. The mean pressure is about 8 per cent. higher in men than in the other three groups; this may be related to the hæmoglobin, which is about 12 per cent. higher in men than in the others. There is no relationship to weight, height, respiratory capacity, or muscular work. There are slight variations occasionally seen in the same person, but no definite diurnal variations.

W. D. H.

Specificity of Precipitins. ANDREW HUNTER (*J. Physiol.*, 1905, 32, 327—342. Compare Abstr., 1903, ii, 663).—The albumin, euglobulin and pseudoglobulin of ox-serum are each capable of leading to the formation of precipitins, and these are in a limited degree specific. The precipitins thus obtained are mixtures of at least four distinct anti-substances, of which albumin yields one only, whilst euglobulin and pseudoglobulin each yield three. The production of precipitins follows a wave-like course, and is accompanied by an intermittent leucocytosis, the number of leucocytes at any moment bearing an inverse relation to the amount of precipitin.

W. D. H.

Precipitins for Snake Venoms and Snake Sera. ANDREW HUNTER (*Proc. Physiol. Soc.*, 1905, lxi—lxii; *J. Physiol.*, 32).—Injection of various venoms causes the appearance in the serum of specific precipitins. The haptophore groups of cobra venom and daboia venom are thus shown to be very different. The precipitin reaction cannot be used to standardise venoms and antivenoms, for the precipitability of any venom by its antivenom is quite independent of its toxicity.

W. D. H.

Pigmentation and Intravascular Coagulation. GEORGE P. MUDGE (*Proc. Physiol. Soc.*, 1905, lxxviii; *J. Physiol.*, 32).—Nucleo-proteid was prepared from rabbits' testes. A larger dose is required to kill albino rabbits than pigmented animals, whether the nucleo-proteid was obtained from albino or pigmented animals. In a certain proportion of cases, intravascular coagulation failed to occur in albinos when injected with a nucleo-proteid derived from pigmented animals, although the injection produced death from some other cause (confirmatory of Halliburton and Brodie, *J. Physiol.*, 1894, 17, 135—173; Abstr., 1894,

ii, 463; Pickering, *J. Physiol.*, 1896, 20, 310—315; Abstr., 1896, ii, 664).
W. D. H.

Changes in Viscosity of Blood during Narcosis. RUSSELL BURTON-OPITZ (*J. Physiol.*, 1905, 32, 385—389. Compare this vol., ii, 98).—Dogs were anaesthetised with morphine in conjunction with either ether or chloroform. The viscosity of the blood is increased by deep and lessened by light narcosis. The differences found with moderate narcosis are too slight to be of any practical importance. With ether, the specific gravity varies with the viscosity; with chloroform, an inverse relationship exists.
W. D. H.

Gaseous Metabolism of Rabbits' Small Intestine. A. E. BOYCOTT (*J. Physiol.*, 1905, 32, 343—357).—Oxygen disappears from the intestine partly by diffusion, but mainly by being used up by the mucous membrane. There is very little direct exchange with the blood. It is usually present in the small intestine. The intestinal wall is very permeable to carbon dioxide. In the rabbit the permeability is so great that the tension of the gas within the intestine is nearly the same as that outside. The nitrogen of air introduced into the intestine undergoes very little change in five hours; there is a small, but doubtful, loss by diffusion. The combustible constituents of the intestinal gas are of a complex and partly unknown nature; they may enter the lumen of the gut from the blood. An appendix gives some analyses made of the gases found naturally in the intestine of cats and dogs; carbon dioxide, oxygen, nitrogen, hydrogen, and methane were present.
W. D. H.

Carbohydrate Metabolism in Partially Depancreated Dogs. PERCY W. COBB (*Amer. J. Physiol.*, 1905, 14, 12—15).—The experiments were in some cases followed by glycosuria; in some cases, duodenal abscesses were found *post mortem*. The dextrose-nitrogen ratio was high. The sugar from endogenous proteids appears to be more readily oxidised by the tissues than is that derived from exogenous proteids. Lüthje (*Münch. med. Woch.*, 1903, 50, 1539) takes the same view.
W. D. H.

Animal Lactase. CH. PORCHER (*Compt. rend.*, 1905, 140, 1406—1408).—A good agent for extracting lactase from the intestinal mucous membrane of freshly killed kids was found to be ether saturated with water.
W. D. H.

Amylolytic Action of Urine. GEORGE H. CLARK (*Glasgow Med. J.*, 1905, June).—The amylolytic enzyme in urine, which has been described by several previous observers, is precipitable by alcohol and is soluble in glycerol. It was not found in five cases of diabetic urine.
W. D. H.

The Specificity of Certain Digestive Ferments. K. KIESEL (*Pflüger's Archiv*, 1905, 108, 343—368).—The proteolytic and rennetic ferments of the dog and cow show some specificity in relation to the

caseinogen yielded by the two animals respectively. Trypsin and pancreaticrennet are exceptions to this rule, and show a constant greater affinity for the caseinogen of the cow. Differences between the caseinogen of various animals have long been known. It now appears that there are molecular differences in the ferments which attack it. The specificity of the gastric ferments emphasises the importance of feeding young animals on the milk of their mothers. Cow caseinogen by heating to 90° becomes partly insoluble in alkalis; this does not occur in the case of dog's milk, but the caseinogen of this animal after such treatment unites with more alkali. The time law for pancreatic rennet is the same as that described by Segelcke and Storch for gastric rennin.

W. D. H.

Action of Trypsin. SVEN G. HEDIN (*J. Physiol.*, 1905, 32, 465—485).—The time of digestion varies inversely with the amount of trypsin, provided the substrate (various proteids were tried) is present in sufficient quantity.

W. D. H.

Antitryptic Action of Serum Albumin. SVEN G. HEDIN (*J. Physiol.*, 1905, 32, 390—394).—The antitryptic action of serum has been shown to be connected with the albumin fraction. If trypsin and antitrypsin are added separately to the substrate (casein), the order in which they are added is a matter of indifference. If they are mixed before they are added, then the neutralising effect of the antitrypsin is greater than if they are added separately. The longer the mixture is kept before it is added to the substrate, the greater up to a certain point is the amount of trypsin neutralised, especially at high temperatures (37°). Trypsin neutralised at such a temperature is not even partly activated on lowering the temperature.

W. D. H.

Glycolytic Principle in Blood-Fibrin. NADINE SIEBER (*Zeit. physiol. Chem.*, 1905, 44, 560—579).—The occurrence of glycolysis depends on a high relative proportion between the active principle and the sugar acted on. Bacterial action can be excluded.

W. D. H.

Localisation of Ferments in the Hen's Egg. JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1905, 44, 540—545).—By the autolytic method, ferments were found to be absent in the white; but in the yolk, ferments able to decompose proteid, lecithin, and fat are present.

W. D. H.

Hours of Sleep in Public Schools. THEODORE DYKE ACLAND (*Lancet*, 1905, ii, 136—142).—A plea on physiological grounds for longer hours of sleep than are allowed by traditional rules in English public schools. Metabolism is relatively more active in growing persons, and so more rest is necessary. Growing chiefly occurs during sleeping hours. In some schools in America the necessity for about ten hours of sleep for boys seems to have been already recognised.

W. D. H.

Chemistry of Flesh. II. HARRY S. GRINDLEY and A. D. EMMETT (*J. Amer. Chem. Soc.*, 1905, 27, 658—678. Compare Abstr., 1904, ii, 829).—The paper treats mainly of methods. The examination of cold-water extracts (in raw meat, from a fourth to a third of the total solids is soluble in this reagent) gives a truer notion of the composition of flesh than the older methods do. The proteids differ in character and quantity in different meats; among them albumose is present. A point is made of the high percentage of extractives: in beef this is from 1 to 1.7 for nitrogenous, and from 1.4 to 2.2 for non-nitrogenous extractives. The differences between raw and cooked meats are emphasised. The paper contains numerous analytical tables.

W. D. H.

Heat Value of Nervous and Muscular Tissues in Guinea Pigs of Different Age. J. TRIBOT (*Compt. rend.*, 1905, 140, 1565—1566).—The amount of fatty matter reaches its maximum in the guinea pig on the 120th day after birth in the nervous tissues, and on the 180th day in the muscles; the proteid matter reaches a minimum on the same dates. The net result is an increased calorific value of the material at the same times.

W. D. H.

So-called Normal Arsenic. ADAM J. KUNKEL (*Zeit. physiol. Chem.*, 1905, 44, 511—529).—Gautier's statement that arsenic must be regarded as a normal constituent of animal tissues and organs is questioned. In the present research it was never found in any organs, even in the thyroid, to which Gautier attaches special importance. Much of the present paper relates to methods of analysis.

W. D. H.

An Instrument for recording Ciliary Activity. WALTER E. DIXON and O. INCHLEY (*J. Physiol.*, 1905, 32, 395—400).—The instrument, which is described and figured, is called the cilioscribe. The ciliary activity ultimately rotates a drum on which a time tracing is taken; the comparative rate of ciliary action is thus known. Details of the best saline fluids to use to moisten the ciliated surface are given. The instrument can be used to study the effect of temperature, drugs, &c., on ciliary movement.

W. D. H.

Reversal of the Effective Stroke of Cilia. G. H. PARKER (*Amer. J. Physiol.*, 1905, 14, 1—6. Compare this vol., ii, 183).—Revision of previous conclusions is rendered necessary by the following new observations: reversal of the effective stroke in the labial cilia of sea anemones is produced by creatine, but not by creatinine or uric acid. It is probable that creatine is an effective element when fish meat is applied to the lips of these animals. No reversal is obtained with sucrose, dextrose, lactose, or maltose, but it is produced by Witte's peptone, deuterio-albumose, and aspartic acid. In all instances reversal is not accompanied by discharge of nettle capsules or slime, and so resembles what occurs in normal feeding. The reversal in normal feeding is now held to be due to organic molecules, and not to ion action, although potassium ions in sufficient concentration will cause reversal.

W. D. H.

The Behaviour of Stereoisomerides in the Animal Organism. II. Inactive Amino-acids. JULIUS WOHLGEMUTH (*Ber.*, 1905, 38, 2064—2065. Compare Abstr., 1902, ii, 336).—If an externally compensated amino-acid is given to rabbits by the mouth, subcutaneously, or intravenously, the component which occurs in the animal is digested to its assimilation limit, whilst the other is excreted completely or almost completely in the urine. The excreted tyrosine from 8 grams of *i*-tyrosine given by the mouth consisted of 75 per cent. of the *d*- and 25 of the *l*-amino-acid; of 10 grams of *i*-leucine and of 6 grams of *i*-asparagine, only the *d*-amino-acids, and from 5.5 grams of *i*-glutamic acid only the *l*-component, reappeared in the urine.
G. Y.

Fate of Glyoxylic Acid in the Animal Organism. HANS EPPINGER (*Beitr. chem. Physiol. Path.*, 1905, 6, 492—501).—Although glyoxylic acid is an important factor in plant physiology (Brunner and Chuard, *Ber.*, 1886, 19, 595; Königs, Abstr., 1892, 695; Döbner, 1901, i, 188), little is known of its behaviour in the animal system. A delicate test for glyoxylic acid is Hopkins' indole reaction in the presence of concentrated sulphuric acid, when a red ring is obtained which gradually spreads upwards through the liquid. The red compound can be extracted with amyl alcohol.

No ordinary compounds give this reaction except condensation products of glyoxylic acid when hydrolysed. If indole is replaced by scatole, a green ring is formed.

The following products when oxidised and distilled give the test for glyoxylic acid: ethyl alcohol, lactic, tartaric, and glycollic acids, glycol, glycerol, betaine, and sarcosine. Methyl alcohol, acetone, carbamide, and formic and oxalic acids do not appear to yield glyoxylic acid.

In testing for glyoxylic acid in urine, it is advisable to acidify the urine with phosphoric acid, to distil, and to test the distillate by means of the indole or scatole reaction. Crude urine does not give the latter reaction.

The urine of many animals gives the indole test, but occasionally negative results are obtained; the differences are probably due to divergencies in feeding, although the introduction of calcium glyoxylate into the food does not increase the amount of glyoxylic acid in the urine. The administration of considerable amounts of alcohol (10—15 c.c.) increases the glyoxylic acid to a large extent, and to a less extent the administration of glycine, glycollic acid, betaine, and sarcosine.

When glyoxylic acid is given to dogs, a considerable increase in the oxalic acid and allantoin contained in the urine is observed.

J. J. S.

Influence of Fruit on the Precipitation of the Uric Acid of the Urine. WILLIAM J. SMITH JEROME (*Lancet*, 1905, ii, 142—147).—Pears, grapes, figs, oranges, and dates may be taken not only with impunity but with advantage by those who suffer from calculus and gravel. The good effect is due to the lessened acidity of the urine.

W. D. H.

Experimental Glycosuria. JOHN J. R. MACLEOD and J. DOLLEY (*Proc. Physiol. Soc.*, 1905, lxxiii—lxiv; *J. Physiol.*, 32).—Eckhard found that puncture of the medulla oblongata did not cause glycosuria when the splanchnic nerves were cut, and so argued that the impulses reached the liver by these nerves. Glycosuria does not follow stimulation of the peripheral end of the cut nerves, but it does occur if the cervical part of the spinal cord is stimulated; hence the impulse is considered to undergo some change as it passes through the upper sympathetic ganglia. In the present research, nicotine was injected to block the ganglia; puncture then produces little or no glycosuria, and glycogen did not disappear from the liver. Stimulation of the central end of the vagus produces glycosuria, whether nicotine has been injected or not. Application of nicotine locally to the stellate ganglia during excitation of the vagus renders the urine sugar-free. It also causes a lowering of blood pressure, and that in itself causes the sugar to disappear.

W. D. H.

Metabolism in Cystinuria. CARL ALSBERG and OTTO FOLIN (*Amer. J. Physiol.*, 1905, 14, 54—72).—The experiments recorded in connection with a case of cystinuria do not corroborate the views of Loewi and Neuberg (this vol., ii, 103) on this subject. With a standard (Voit) diet of milk and egg, the neutral sulphur, including the cystine sulphur of the urine, was about five times as great as the normal; this is produced chiefly or wholly by the presence of cystine, and occurs at the expense of the inorganic sulphates; the ethereal sulphates occur in normal proportions. This is accompanied by a fall in ammonia to about half the normal quantity, and a reduction of about 4 per cent. in the urea nitrogen. The elimination of uric acid and creatinine is normal. The "undetermined" nitrogen is increased. It appeared probable, therefore, that amino-acids might account for this, and that Loewi and Neuberg's generalisations on the nature of the disease were correct. This interpretation was shattered by the results obtained when a fat and starch diet was substituted for the one first used, for the undetermined nitrogen remained stationary. If aspartic acid was added to the nitrogen-free diet, the nitrogen excreted rose to an amount beyond that which the aspartic acid would account for, and the increase is due to urea and not to undetermined nitrogen; the patient was therefore able to convert the nitrogen of aspartic acid into urea. If pure cystine prepared from hair was added instead, the neutral sulphur elimination was not increased; that is to say, in so far as cystine is absorbed it is not excreted as such, but as ordinary sulphates. There is thus no inability to katabolise normally the usual products of proteolysis. There is less neutral sulphur excreted when the diet contains little or no proteid; patients suffering from cystinuria should therefore keep their proteid intake at a minimum. The cystine which is eliminated is not absorbed as such from the alimentary tract; that comes from other or larger sulphur complexes; it is this and the sulphur from the tissues which the cystinuric person is unable to convert into sulphates. No support is given to the view that calculus-cystine differs structurally from proteid-cystine (compare Rothera, this vol., ii, 267).

W. D. H.

Migration of Potassium and the Injury Current. J. S. MACDONALD (*Proc. Physiol. Soc.*, 1905, lxvi—lxvii; *J. Physiol.*, 32).—At an injured spot of the axis cylinder there is a granular appearance, the granules being stainable with neutral-red; Macallum's reagent shows a dense precipitate of potassium salts at the same spot. Injury probably causes a precipitation of proteid matter and a liberation of potassium salts in a state of simple aqueous solution. A new theory of nerve-conduction is founded on this and related facts.

W. D. H.

Photo-electrical Effects in Frog's Eyeball. AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1905, lxvi; *J. Physiol.*, 32).—Certain facts show that the photo-electrical effects are more probably pigmentary than retino-motor. The response is increased by tetanisation up to a certain strength, and even very strong tetanisation does not abolish the photo-electrical response, though it abolishes the "blaze-reaction."

W. D. H.

Action of Salts on Skeletal and Heart Muscle. A. E. GUENTHER (*Amer. J. Physiol.*, 1905, 14, 73—104).—A supply of sodium, calcium, and potassium ions in definite proportions is necessary to the best maintenance of the activity of skeletal and heart muscle. Sodium and potassium produce relaxation and calcium contraction when all three are present together; given alone, their effects are a little different; the order of application makes a difference also. To explain some of the complex results obtained, which are described in full, the assumption has to be made that there are two contractile substances in the sartorius, and three in the heart.

W. D. H.

Action of Optical Isomerides. II. Hyoscines. ARTHUR R. CUSHNY and A. ROY PEEBLES (*J. Physiol.*, 1905, 32, 501—510. Compare Abstr., 1903, ii, 564).—Hyoscine and *r*-hyoscine have the same effect on the central nervous system in man and mammals, and on the motor terminations in the frog. In the latter animal, they do not affect the central nervous system. On salivary glands and cardio-inhibitory fibres, *l*-hyoscine acts twice as strongly as the racemic base. From this it is inferred that *d*-hyoscine acts equally strongly on the central nervous system, but has no action on secretory or on cardio-inhibitory nerve fibres. *d*-Hyoscine differs from *d*-hyoscyamine in not stimulating the frog's spinal cord; this may be due to its being so rapidly excreted. Hyoscyamine is devoid of hypnotic action in man when given in doses which do not affect the peripheral organs.

W. D. H.

Action of Adrenaline. T. R. ELLIOTT (*J. Physiol.*, 1905, 32, 401—467).—A full account of experiments previously published (Abstr., 1904, ii, 577. Compare also *ibid.*, 832).

W. D. H.

Physiological Action of Chrysotoxin. H. H. DALE (*Proc. Physiol. Soc.*, 1905, lviii—lx; *J. Physiol.*, 32).—Chrysotoxin, the active substance of ergot, was injected intravenously in cats. Small doses cause effects similar to those produced by stimulation of sympathetic

nerves (including cranial and sacral autonomic nerves); the seat of stimulation is either the ganglion cells or the endings on them of preganglionic fibres. Larger doses paralyse motor nerve-endings except those of the cranial and sacral autonomic groups; there is no paralysis of inhibitory endings. Whether the same substance is responsible for both classes of effects is doubtful. The paralytic effects permit a new method of discrimination in cases where an organ receives both motor and inhibitory impulses from the sympathetic.

W. D. H.

Action of Drugs on the Paralysed Iris. HUGH K. ANDERSON (*Proc. Physiol. Soc.*, 1905, xlix—1; *J. Physiol.*, 32).—After excision of the ciliary and accessory ciliary ganglia, eserine has no effect on the pupil, but pilocarpine causes constriction; the latter effect is annulled by atropine as in the normal eye. Atropine and pilocarpine probably combine with some substance in the sphincter, but atropine has the greater affinity for it. This material is not in the contractile substance, because atropine does not prevent pupillary contraction after death or during asphyxiation. It is not in the nerve fibres as the effect is observed after nerve-degeneration. It must therefore be in the nerve-ending. This connecting link must be composed of two parts, a nervous part excited by eserine, which degenerates after cutting the ciliary nerves, and a muscular portion containing the substance on which atropine and pilocarpine act.

W. D. H.

Detection of Morphine in Cases of Poisoning. H. WEFERS BETTINK (*Chem. Centr.*, 1905, i, 1421—1422; from *Pharm. Weekblad*, 42, 302—307).—In a case of morphine poisoning, death occurred after two days notwithstanding the speedy application of the stomach-pump. Morphine hydrochloride crystals were isolated from the contents of the stomach and intestines. No such crystals could be isolated from the blood, spleen, or kidneys, but satisfactory colour reactions were obtained. No morphine could be detected in the brain and liver. The body contained no urine, so this could not be examined. The author thinks that the decided quantity of morphine still present in the stomach, notwithstanding the defæcation, must have deposited from the blood.

L. DE K.

Chemistry of Vegetable Physiology and Agriculture.

Action of Some Soil Micro-organisms on Ammonium Sulphate and Sodium Nitrate. ALBERT STUTZER and W. ROTHE (*Bied. Centr.*, 1905, **34**, 433—434; from *Fühling's landw. Zeit.*, 1905, **53**, 629).—Experiments with eight varieties of soil micro-organisms showed that ammonium sulphate is a better food than sodium nitrate, and that the production of organic nitrogen compounds by various soil microbes is especially promoted by the presence of calcium carbonate and ammonia.

As regards the solubility of the nitrogenous matter produced, it was found in the case of *Aspergillus glaucus* that 13·5 per cent. dissolved in

water, 44.3 dissolved in pepsin and hydrochloric acid, whilst 42.2 per cent. was insoluble (nuclein). When asparagine was employed, the proteids produced by *Aspergillus glaucus* contained 81 per cent. of insoluble substance (nuclein). In the case of *Streptothrix odorifera*, the proteids produced from asparagine contained 70 per cent. of insoluble matter.

N. H. J. M.

Action of Ammonium Salts on the Nitrification of Sodium Nitrite by the Nitric Ferment. E. BOULLANGER and L. MASSOL (*Compt. rend.*, 1905, 140, 687—689. Compare Abstr., 1904, ii, 361).—One per thousand of sodium carbonate is not necessary to the nitric ferment and may be reduced to 0.2 per thousand in Winogradsky and Omeliansky's medium. When the amount does not exceed 0.25 gram per litre, the duration of the conversion of nitrite is not affected by the presence or absence of ammonium sulphate. The injurious action observed by Winogradsky and Omeliansky is attributed to free ammonia liberated by the 0.1 per cent. sodium carbonate; with less sodium carbonate, the ammonia liberated is insufficient to have an injurious action.

N. H. J. M.

Yeast Catalase. W. ISSAEW (*Zeit. physiol. Chem.*, 1905, 44, 546—559).—Salts and alkalis act catalytically in the reaction; they have an optimum concentration. Potassium compounds act more favourably than sodium compounds. Weak alkalis extract more catalase from yeast than water. Acids and iodine destroy catalase. The action of catalase increases with the amount present, but not in exact proportion; the increase in action is shown.

W. D. H.

Non-inverting Yeasts. HENRI VAN LAER (*Centr. Bakt. Par.*, 1905, ii, 14, 550—556).—Non-inverting aërobic yeasts, in which the life of the "vegetating yeast" dominates, may become inverting. The sucrose utilised for their nutrition undergoes inversion before it is consumed. In the case of *Mycoderma cerevisiae* this does not manifest itself owing to the oxidising power, which is independent of the inversion, predominating.

N. H. J. M.

Autodigestion of some Varieties of Yeast. MARTIN SCHENCK (*Chem. Centr.*, 1905, i, 1570—1571; from *Woch. Brau.*, 22, 221—227).—The products of the autodigestion of brewers' yeast and spirit yeast are similar, but in the latter case arginine does not occur, being probably decomposed into tetramethylenediamine, if it pre-exists at all in the proteid substances. Extracted yeast cells become brown or black when exposed to air; only those of spirit yeast seem to remain colourless.

N. H. J. M.

Production of Hydrogen Sulphide by Yeast. HERMANN WILL and F. SCHÖLLHORN (*Chem. Centr.*, 1905, i, 1570; from *Zeit. ges. Brauw.*, 23, 285—287).—The production of hydrogen sulphide was observed in a "special Pilsen beer" and is attributed to weakening of the Pilsen yeast, resulting in an alteration of its character, the power of producing hydrogen sulphide being induced by addition of gypsum.

N. H. J. M.

Production of Acetic Acid in Alcoholic Fermentation.

RUDOLF REISCH (*Centr. Bakt. Par.*, 1905, ii, 14, 572—581).—The production of acetic acid in alcoholic fermentation is directly connected with the biological activity of the yeast and only takes place during fermentation. Addition of alcohol is without effect, whilst a small amount of acetic acid entirely checks the production of acetic acid and may even result in a loss of acetic acid possibly owing to some of it forming ethyl acetate.

N. H. J. M.

Occurrence in Soil of Fungi causing Alcohol Fermentation.

EMIL CHR. HANSEN (*Centr. Bakt. Par.*, 1905, ii, 14, 545—550. Compare *ibid.*, 10, 1).—It is shown that the soil is the most important resort in the winter, and that it is the chief source of the micro-organisms at all times of the year.

N. H. J. M.

Action of the Radiations from Radium Bromide on some Organisms.

HENRY H. DIXON and J. T. WIGHAM (*Sci. Proc. Roy. Dubl. Soc.* 1904, 10, 178—192).—The experiments indicate that the radiations from radium bromide do not interfere to any marked extent with the metabolism of cells of *Lepidium sativum* and *Volvox globator*. On the other hand, the bacteria *Bacillus pyocyaneus*, *B. prodigiosus*, *B. typhosus*, and *B. anthracis*, when exposed to the radiations at no great distance from the tube, were found to be inhibited in their development, and in some cases perhaps killed. It is possible that the negative electrons from the radium bromide attach themselves to the positive hydrogen ions of the cultures, thus setting free hydroxyl ions. The consequent alkalinity would check the action of the enzymes on which the metabolism of the cells depends, for the action of all enzymes, trypsin excepted, is inhibited in an alkaline solution.

J. C. P.

Comparative Assimilability of Ammonium Salts, Amides,

Amines, and Nitriles. L. LUTZ (*Compt. rend.*, 1905, 140, 665—667. Compare Abstr., 1898, ii, 530, and 1900, ii, 233).—Results obtained with *Aspergillus niger*, *Aspergillus repens*, and *Penicillium glaucum* showed that amides are the most readily assimilable nitrogenous compounds, giving higher results than Raulin's solution containing ammonium salts. Amines are somewhat less assimilable and nitriles much less.

The assimilability of amines is in inverse relation to their molecular weight.

N. H. J. M.

Mutual Action of Salts in the Mineral Nutrition of

Plants. P. KOSSOWITSCH (*Bied. Centr.*, 1905, 34, 378—384; from *Journ. exper. Landw.*, 1904, 5, 598).—Plants are able to utilise nitrogen both in the form of ammonium salts and as nitrates. When nitrates are employed, the plant takes up more acid than base, leaving an alkaline substratum which, if not neutralised by some other constituent of the substratum, may cause injury to the development of the plant. In the case of ammonium salts, the plant utilises more base than acid,

so that an acid substratum results unless calcium carbonate, for instance, is present. The acidity thus produced will, if it reaches a certain point, be injurious to the plant; at the same time, however, it acts as a solvent and thus supplies an increased amount of mineral matter. When both forms of nitrogen are supplied (in ammonium nitrate), the reaction of the substratum is not essentially affected and the conditions are favourable for normal growth.

N. H. J. M.

Estimation of the Carbon Dioxide given off by Roots during their Development. P. KOSSOWITSCH (*Bied. Centr.*, 1905, **34**, 367—372; from *Journ. exper. Landw.*, 1904, **5**, 493).—The amount of carbon dioxide given off by mustard roots is very considerable in relation to the amount of ash constituents in the plant. It is doubtful whether the carbon dioxide only acts on the soil or whether it has other functions.

N. H. J. M.

Action of Vegetable Acids on Phosphates. ANTONIO QUARTAROLI (*Chem. Centr.*, 1905, **i**, 1699—1610; from *Staz. sper. agrar. ital.*, **38**, 83—113).—The organic acids which usually occur in plants first render insoluble phosphates soluble and then convert them into dihydrogen phosphates. Any free phosphoric acid which may be produced is converted, in the plants, into a dihydrogen salt. This is explained by the lower acidity of organic acids as compared with phosphoric acid, and by their greater affinity as compared with acid phosphates.

N. H. J. M.

Proteid Formation in Ripening Seeds. W. ZALESKI (*Chem. Centr.*, 1905, **i**, 1605—1606; from *Ber. deut. bot. Ges.*, **23**, 126—133).—The increase in proteids in ripening peas is coincident with a decrease in the amounts of amino-acids, amides, and organic bases. Albumoses are formed from amino-substances as an intermediate product.

The chemical process in ripening is the reverse of that which occurs in germination.

N. H. J. M.

Proteolytic Enzyme of Ripening Seeds. W. ZALESKI (*Chem. Centr.*, 1905, **i**, 1606—1607; from *Ber. deut. bot. Ges.*, **23**, 133—142).—The proteolytic enzymes of pea seeds act in acid, but better in slightly alkaline solutions, and are very sensitive towards further additions of alkaline carbonates. In the auto-digestion of unripe pea seeds, the decomposition of proteids is accompanied by the production of amino-acids which were not identified. Albumoses and peptones are not formed, or do not accumulate, being very readily digested by the pea-preparation. It is uncertain whether the ripening seeds contain only one ferment of a tryptic nature or whether they contain several, including trypsin.

N. H. J. M.

Successive Distributions of Estragole and Terpenic Compounds among the Different Organs of an Annual Plant. EUGÈNE CHARABOT and G. LALOUE (*Compt. rend.*, 1905, **140**, 667—669. Compare Abstr., 1904, **ii**, 365).—During the period preceding the

appearance of the first flowers there is an accumulation in the green leaves of an essential oil poor in estragole and rich in terpenic compounds. The first flowers contain a less soluble essence containing more estragole. When the flowering period is advanced, the amount of essential oil diminishes in the green parts and increases in the flowers; at the same time the solubility of the oil in the green parts of the plant diminishes. By the time that the seed has ripened there is loss of essential oil in the flowers and a gain in the leaves; the oil becomes richer in terpenic compounds and more soluble. There is, however, no decrease in the solubility of the essential oil of the flowers.

N. H. J. M.

Fly Agaric (*Amanita Muscaria*). II. JULIUS ZELLNER (*Monatsh.*, 1905, 26, 727—747. Compare Heinisch and Zellner, *Abstr.*, 1904, ii, 678).—The acid number of this fungus increases from 38.22 for freshly gathered material to 180.00 for dried twelvemonth-old material; this increase, which is practically complete in four months, during which time about 78 per cent. of the fat present is hydrolysed, is due to the action of a ferment. This is insoluble in water, is not affected by removal of the fat by extraction with light petroleum, and brings about a slow but far-reaching hydrolysis of foreign fats (rape-seed, olive, or castor oils, cocoa butter, or tallow) with which it is mixed. The ferment is best used in the form of the freshly dried and ground fungus; its action is not affected by the addition of small quantities of dilute sulphuric acid or of ammonia.

In addition to the substances previously mentioned, propionic and fumaric acids and amanitole have now been obtained from the fungus.

Amanitole is obtained in small quantity on distilling the fungus with steam; it forms colourless, oily drops which solidify to white, flocculent crystals, melts at 40°, has a neutral reaction, is soluble in ether or light petroleum, but is insoluble in aqueous alkali hydroxides.

Ergosterin, which occurs in the fungus to the extent of 0.1—0.2 per cent., crystallises from alcohol in rhombic leaflets which occasionally appear monoclinic, or from benzene, light petroleum, acetone, or carbon disulphide in slender needles. It is soluble in methyl alcohol or chloroform. When shaken with chloroform and sulphuric acid, it gives with the latter a red coloration, which, on dilution with water, becomes green and finally blue, the chloroform remaining colourless (compare Tanret, *Abstr.*, 1889, 407); with acetic anhydride and concentrated sulphuric acid, ergosterin gives a purple coloration which becomes blue and, on addition of water, emerald-green.

The supposed lichenstercic acid found in fly agaric by Bolley (*Annalen*, 1853, 86, 44) was probably impure palmitic acid. Two substances from fungus have been named agaricin; Gobley's substance obtained from mushrooms (*J. Pharm. Chim.*, 1856, [iii], 29, 81) was probably ergosterin, whilst Schoonbrodt's (*Jahresber.*, 1864, 613) was mannitol.

G. Y.

Comparative Experiments on the Manuring of Beet. KARL ANDRLIK, VL. STANEK, and B. MYSÍK (*Zeit. Zuckerind. Böhm.*, 1905, 29, 261—285 and 323—349).—The authors have carried out experi-

ments on the manuring of beet with Chili saltpetre, potassium chloride, potassium sulphate, superphosphate, mineral phosphate, and Thomas slag. The roots, leaves, and leaf-stalks of each crop were separated and examined, and the influence determined of the manures separately and of their various combinations on the ash and its composition, the "harmful ash" (that part which is not eliminated in the extraction of sugar), the quantity and nature of the nitrogenous substances, the sugar-content of the beet, and the purity of the expressed juice. For the detailed results, reference must be made to the original.

In general, large additions of any of the above manures by itself injure the quality of the beet, and cause the beet to take larger quantities of the remaining nutrient materials from the soil. Where the manuring mixture contains all the food-materials required, those administered in excess do not accumulate to any great extent in the roots; the plants, and especially the roots, endeavour to maintain certain relations between the different manure constituents absorbed.

T. H. P.

Potassium Manuring. PAUL WAGNER, R. DORSCH, H. RUTHS, and G. HAMANN (*Bied. Centr.*, 1905, **34**, 435—446; from *Arb. deut. landw. Ges.*, 1904, Heft 96).—Potassium salts containing much chlorine considerably increased the amounts of chlorine in barley, beet, and especially in the leaves of mangolds and potatoes. Rye grain, which contains only a little chlorine, is not influenced.

The results of numerous field experiments on the relative values of kainite and 40 per cent. potassium salts were in favour of kainite both in the case of arable and meadow land.

N. H. J. M.

Analytical Chemistry.

Tube Apparatus for Drying in a Current of Carbon Dioxide. KARL VOIGT (*Chem. Zeit.*, 1905, **29**, 691—692).—A modification of the apparatus described by Ulsch (*ibid.*, 1895, **19**, 1183) so as to render it more suitable for drying the substance in a current of carbon dioxide. Full illustrations are given. L. DE K.

Modification of Bohr's Gas Receiver. JOSEPH BARCROFT (*Proc. Physiol. Soc.*, 1905, 1—li; *J. Physiol.*, **32**).—A simplified and efficient form of receiver for use in analysis of blood gases is described and figured. W. D. H.

Standardising of Normal Acids. JOHN SEBELIEN (*Chem. Zeit.*, 1905, **29**, 638—642).—The substance best suited for standardising acids is pure dry sodium oxalate, a weighed quantity of which is converted into carbonate by heating over a spirit lamp (Sørensen's process).

For the details of precautions needful and of the experiments made to determine the various sources of error, the original must be consulted.

L. DE K.

Use of Benzene or Toluene as Indicator in Iodometry.

BENJAMIN M. MARGOSCHES (*Zeit. anal. Chem.*, 1905, 44, 392—395).—With regard to the use of benzene for this purpose (this vol., ii, 280), the author points out that Moride recommended benzene as an indicator as long ago as the year 1852 (*Compt. rend.*, 1852, 35, 789).

W. P. S.

Estimation of Fluorine. JULIUS SCHUCH (*Chem. Centr.*, 1905, i, 1617; from *Zeit. landw. Vers. Wes. Öst.*, 9, 531—549).—A critical investigation of the various recognised processes for the estimation of fluorine. The processes most suitable are the volumetric process of Offermann (Abstr., 1891, 615) and the gasometric method of Hempel and Scheffler (Abstr., 1899, ii, 380).

L. DE K.

Estimation of Sulphur in Iron Ores, Slags, and Lime.

H. HARTWIGSSON (*Chem. Centr.*, 1905, i, 1616; from *Stahl u. Eisen*, 25, 542—543).—The sample is ignited in a current of pure hydrogen, and any hydrogen sulphide formed is absorbed in two Erlenmeyer flasks containing a solution of cadmium acetate in dilute acetic acid. The reduced mass is then dissolved in dilute hydrochloric acid in a flask from which the air has been expelled previously by a current of carbon dioxide, and the resulting hydrogen sulphide is then passed into the same cadmium solution. The cadmium sulphide formed is estimated iodometrically as usual.

L. DE K.

Estimation of Sulphur in Roasted Pyrites. B. N. GOTTLIEB (*Chem. Zeit.*, 1905, 29, 688—689).—A reply to Jene (this vol., ii, 350). The accuracy of the acid process may be interfered with by the presence of barium or lead compounds. If any free sulphur should separate on treating the sample with nitro-hydrochloric acid, a little bromine should be added. If it is desired to ascertain the total amount of sulphur, including that existing as earthy sulphates, the fusion method should be resorted to. The operation may be conducted in an iron crucible.

L. DE K.

Estimation of Combined Sulphuric Acid[in Waters]. C. BLACHER and U. KOEBER (*Chem. Zeit.*, 1905, 29, 722—723).—One hundred to two hundred c.c. of the sample are boiled down to about 25 c.c. and 20—40 c.c. of *N*/10 alkali (containing equal parts of sodium hydroxide and sodium carbonate) are added. After boiling, the liquid is filtered and the precipitate washed with a mixture of 10 c.c. of water and 10 c.c. of the alkaline solution. The filtrate is mixed with phenolphthalein, boiled, decolorised with hydrochloric acid, and concentrated to 25 c.c. Seventy to ninety c.c. of alcohol are added, the mixture is heated to boiling, neutralised with potassium hydroxide, and then exactly decolorised with *N*/10 hydrochloric acid. After adding 0.5 c.c. of *N*/10 sodium carbonate, the liquid is titrated with *N*/10 barium

chloride until it has become nearly colourless. Another 9.5 c.c. of *N*/10 sodium carbonate is added, the liquid is again heated to boiling, and the titration with barium chloride is continued to the end. One c.c. is then deducted, being due to sodium carbonate. L. DE K.

Nitrogen Estimations in Lysine and Analogous Substances by Kjeldahl's Method. S. P. L. SÖRENSEN and A. C. ANDERSEN (*Zeit. physiol. Chem.*, 1905, 44, 429—447. Compare Kutscher and Steudel, *Abstr.*, 1903, ii, 687; Sørensen and Pedersen, *ibid.*, 1904, ii, 83).—The low results obtained in estimating nitrogen in lysine by the Kjeldahl method are not due, as stated by Henderson, Kutscher, and others, to the evolution of hydrogen cyanide during the heating with concentrated sulphuric acid, but rather to the formation of piperidine-2-carboxylic acid.

Good results have been obtained by the ordinary Kjeldahl method with pyrrolidine-2-carboxylic acid, α -amino- δ -hydroxyvaleric acid, $\alpha\delta$ -diaminovaleric acid, $\alpha\delta$ -diaminoadipic acid, all such compounds as can yield a cyclic compound containing four carbon and one nitrogen atom.

Pyridine, piperidine, lysuric acid, dibenzoyl-lysine, and ethyl trimethylenediphthaliminomalonate all give low results by the ordinary method, but yield good results when Gunning's (*Abstr.*, 1889, 796) or Arnold and Wedermeyer's modification (*ibid.*, 1892, 1517) is employed (compare Bredig and Brown, *Abstr.*, 1904, ii, 247).

Compounds which contain a CO group in place of a CH₂ group in the piperidine ring give theoretical yields by the ordinary Kjeldahl method; examples are Gabriel's ethyl γ -phthaliminopropylmalonate (*Abstr.*, 1890, 1129; 1891, 948), piperidone, and also γ -aminopropylmalonic acid.

α -Aminoadipic acid can be analysed by the ordinary Kjeldahl method with good results. J. J. S.

Assay of High-grade Nitric Acid. F. WINTERER (*Chem. Zeit.*, 1905, 29, 689).—An improved table showing the percentage of real nitric acid (HNO₃) corresponding with the sp. gr. (or degree Beaumé) of the sample. The sp. gr. ranges from 1.485 to 1.520. L. DE K.

Titration of Nitrous Acid with Quadrivalent Cerium. GIUSEPPE BARBIERI (*Chem. Zeit.*, 1905, 29, 668—669).—The author has noticed that a solution of ceric sulphate is reduced quantitatively to the cerous condition by an alkali nitrite. The reduction proceeds rapidly in the cold, and the end reaction is indicated by the disappearance of the yellow colour. Still better results might be obtained by adding an excess of ceric sulphate and titrating the undecomposed portion with potassium iodide. The cerium solution need not be perfectly free from other metals of the cerium group, but should be checked iodometrically or by von Knorre's method.

L. DE K.

Estimation of Phosphoric Acid. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1905, 18, 953).—A reply to Hlavnicka (this vol., ii, 419), in

which the author upholds the accuracy and suitability of his process (this vol., ii, 284). According to Schucht, the titration with methyl-orange as indicator may be rendered more delicate by the use of a blue glass; the moment acidity is reached the liquid, when viewed through the glass, turns green suddenly.

L. DE K.

Estimation of the Citrate-soluble Phosphoric Acid in Superphosphates. OTTO SEIB (*Zeit. anal. Chem.*, 1905, 44, 397—398).—2.5 grams of the superphosphate are triturated in a mortar with 10 c.c. of a warm mixture of 20 c.c. of sulphuric acid and 80 c.c. of water. The solution is decanted into a 250 c.c. flask, and the trituration repeated three times, the superphosphate being then rinsed into the flask with the remainder of the acid mixture. The flask and its contents are shaken in a shaking-apparatus for 30 minutes, after which the volume is made up to 250 c.c. with water. The solution is filtered and the phosphoric acid estimated in 50 c.c. of the filtrate, as usual, by means of magnesia mixture. The results obtained agree well with those yielded by Petermann's method, the latter being the official method in Belgium.

W. P. S.

Estimation of Boric Acid. KARL WINDISCH (*Zeit. Nahr. Genussm.*, 1905, 9, 641—660).—An interesting and most complete review of the processes recommended in recent times for the estimation of boric acid. As regards the volumetric estimations, it appears that mannitol is preferable to glycerol when titrating with phenolphthalein as indicator, as it is always free from acidity, and does not sensibly increase the bulk of the liquid.

L. DE K.

Estimation of Boric Acid. WILHELM VAUBEL and E. BARTELT (*Chem. Zeit.*, 1905, 29, 629—630).—The well-known glycerol method is recommended. Attention is called to the necessity of titrating with standard potassium hydroxide free from carbon dioxide. If the liquid should contain the latter, it must be expelled by boiling, the flask being covered with a funnel or attached to a reflux condenser.

Phosphoric acid should be absent; other mineral acids are first neutralised, using dimethylaniline-orange as indicator. Sulphurous acid must be expelled by boiling with dilute sulphuric acid. After the final titration with phenolphthalein as indicator, more glycerol should be added to see whether the colour is permanent.

No estimation should be made without a satisfactory reaction being obtained with turmeric paper. The reaction should then be further confirmed by moistening the paper with soda solution, which causes a coloration varying from greenish-blue to greenish-brown, changing to a pure brown on drying. The presence of phosphoric acid somewhat affects the delicacy of the test.

L. DE K.

Detection of Boric Acid in Foods. G. SELLIER (*Ann. Chim. anal.*, 1905, 10, 235—236).—The process is more particularly devised for the detection of borates in substances which it is difficult to reduce

to a white ash, such as white of egg, meat products, &c. Ten grams of the sample are heated in a Kjeldahl flask with 12 c.c. of sulphuric acid until it has dissolved to a dark brown liquid. When partially cooled, 10 c.c. of methyl alcohol are added, the mass is again gently heated, and the escaping vapours are ignited, when the least trace of boric acid will be revealed by the green colour of the flame.

L. DE K.

Estimation and Separation of Silica and Fluorine.

FERDINAND SEEMANN (*Zeit. anal. Chem.*, 1905, 44, 343—387).—In the course of a critical study of the various methods employed for the estimation and separation of silica and fluorine, particularly in cases where they occur together, as in minerals, the author finds that silica is best separated by precipitation with mercuric ammonium carbonate. The latter may be prepared by adding ammonium carbonate to a mercuric chloride solution until the precipitate which forms redissolves, or by digesting freshly precipitated mercuric oxide with an excess of ammonium carbonate solution. The silicate solution, if alkaline, should be nearly neutralised with hydrochloric acid before adding the reagent, and the mixture must be twice evaporated to dryness with the reagent in order to obtain a precipitate which is readily filtered and washed. On ignition, anhydrous silica is obtained. Precipitation of silica by means of ammoniacal zinc solution is not quite trustworthy. The filtrate from the silica-mercury precipitate may be used for the estimation of the fluorine, and for this purpose the methods described by Fresenius, Brandl, Oettel, Carnot, or Offermann are all suitable. The estimation of fluorine as calcium fluoride is not recommended.

W. P. S.

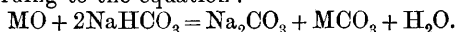
Analysis of Saltpetre. R. BENSEMANN (*Zeit. angew. Chem.*, 1905, 18, 939).—Further minute details as to the assay of Chili saltpetre by means of the oxalic acid process already described (this vol., ii, 481). If a chlorate should be present, it will also be converted into an oxalate, and must be allowed for.

L. DE K.

Estimation of Magnesium and Phosphoric Acid as Magnesium Pyrophosphate. K. K. JÄRVINEN (*Zeit. anal. Chem.*, 1905, 44, 333—342. Compare Abstr., 1904, ii, 515).—For the estimation of magnesia, the following method gives correct results, no excess of phosphate being included in the precipitate. The solution, which should not contain an excessive quantity of ammonium salts, is exactly neutralised, using lacmoid as indicator. A slightly ammoniacal diammonium phosphate solution is then added drop by drop. After a time, when the greater part of the precipitate has separated, 1 per cent. ammonia is added, and then 10 per cent. ammonia in quantity equal to one-third the volume of the whole. The precipitate is collected on a filter at the end of two hours, dried, and ignited over a Bunsen flame, but not over a blast flame. The presence of ammonium oxalate in moderate quantity has no influence on the precipitation.

W. P. S.

A Method in Qualitative Analysis for determining the Presence of certain Metallic Oxides. CHARLES R. C. TICHBORNE (*Sci. Proc. Roy. Dubl. Soc.*, 1904, 10, 331—334).—When certain oxides are either shaken for some time or ground up with a 10 per cent. solution of sodium hydrogen carbonate, the filtered extract gives a deep crimson coloration with phenolphthalein, whereas sodium hydrogen carbonate solution alone gives no colour or only a faint pink. The oxide acting on the acid carbonate produces some of the normal carbonate according to the equation :



The reaction is given readily by litharge, silver oxide, yellow precipitated mercuric oxide, bismuth oxide, stannic oxide, antimony oxide, moist ferrous oxide, precipitated magnetic oxide of iron, precipitated manganous oxide, and zinc oxide (either flowers of zinc, or that obtained by ignition of the carbonate). The reaction is not given by red lead, precipitated mercurous oxide, cupric oxide, alumina, precipitated ferric oxide, or manganese dioxide, whilst with red, crystalline mercuric oxide and cuprous oxide it is not very satisfactory. In general, hydroxides and oxides formed in the moist way bring about the decomposition ; those that have been ignited do not act so well.

J. C. P.

Estimation of Acetic Acid in White Lead. GUSTAVE W. THOMPSON (*J. Soc. Chem. Ind.*, 1905, 24, 487—488).—The author states that the acetic acid often contained in white leads cannot be completely liberated by treatment with dilute sulphuric acid (Lunge's process), and proposes the following method. Eighteen grams of the sample are placed in a 500 c.c. flask arranged for connection with a steam supply and attached to a Liebig's condenser. Forty c.c. of syrupy phosphoric acid, 50 c.c. of water, and 18 grams of zinc dust are added and the whole is distilled to a small bulk. Steam is now admitted until the flask is half filled with condensed water, when the steam is shut off and the contents again boiled down to a small bulk ; this operation is conducted twice. The distillate is then mixed with 1 c.c. of phosphoric acid, and, if necessary, with a little silver phosphate to retain traces of hydrochloric acid, and redistilled. When about 20 c.c. are left in the distilling flask, steam is passed until about 200 c.c. of water has condensed, which is then again boiled down to a small bulk. The operation is repeated until finally 10 c.c. of the distillate requires for neutralisation not more than 0.1 c.c. *N*/10 alkali, using phenolphthalein as indicator. In the titration it will be found convenient to titrate the distillate when it reaches 200 c.c., and then to titrate each subsequent portion of 200 c.c.

L. DE K.

Analysis of Copper Ferrocyanide. AUGUSTE LEUBA (*Ann. Chim. anal.*, 1905, 10, 218—219).—About 0.5 gram of the material is boiled in a reflux apparatus for two hours with a 5 per cent. solution of oxalic acid. The golden-yellow liquid is passed through a filter and the washed precipitate is dissolved in dilute nitric acid, the solution being then added to the main filtrate. After concentrating the liquid on the

water-bath, the iron and copper are separated by the ordinary process. Other metallic ferrocyanides cannot be analysed by the oxalic acid process.

L. DE K.

Separation of Iron from Nickel and Cobalt by Aid of Formic Acid. LEONARD H. BORGSTRÖM (*Chem. Centr.*, 1905, i, 1667; from *Bull. Com. Géol. Finlande*, 1903, No. 14, 1—80. See this vol., ii, 538).

Quantitative Separation of Gold from other Metals by Hydrazine or Hydroxylamine Salts. PAUL JANNASCH and O. VON MAYER (*Ber.*, 1905, 38, 2129—2130).—Gold is precipitated quantitatively from solutions of its salts, whether neutral, acid, or alkaline, by the addition of hydrazine salts. The state of aggregation and the colour of the metal depend largely on the temperature and on the other substances which are present. Hydroxylamine produces a similar effect when used in hydrochloric acid solution at a temperature of 80°; the precipitation, however, proceeds more slowly and for quantitative purposes the mixture must be heated for some time on the water-bath. Gold may be separated from potassium, sodium, barium, strontium, calcium, magnesium, aluminium, chromium, zinc, manganese, iron, uranium, nickel, cobalt, cadmium, mercury, lead, and copper, but not from tin, by these methods.

J. J. S.

Reaction of Hydrazine and Hydroxylamine Salts with Salts of the Platinum Metals and Separation of these from Gold. PAUL JANNASCH and O. VON MAYER (*Ber.*, 1905, 38, 2130—2131).—Gold may be separated from palladium by precipitating the gold with hydroxylamine hydrochloride in hydrochloric acid solution, and then the palladium by means of hydrazine hydrochloride. In a similar manner, gold may be separated quantitatively from platinum, iridium, rhodium, or osmium. Osmium, however, is not completely precipitated by hydrazine in alkaline solution and in acid solution yields no trace of precipitate.

J. J. S.

Physico-chemical Analysis of Soils. H. LAGATU (*Compt. rend.*, 1905, 140, 669—672).—A geometrical method is suggested for interpreting the results of the physical and chemical analyses of soils, a single value being obtained from three variable numbers (as, for instance, clay, fine sand, and coarse sand, or calcium carbonate, clay, and silica) having a constant sum.

N. H. J. M.

Estimation of Alcohol in Beers by means of the Zeiss Immersion Refractometer. EDWIN ACKERMANN and ALBERT STEINMANN (*Chem. Centr.*, 1905, ii, 1672; from *Zeit. ges. Brauw.*, 20, 259—260).—The authors state that the estimation of the alcohol in beers may be effected with advantage by means of the refractometer, and have for this purpose constructed a special table.

The method does not, however, seem suitable for wine distillates.

L. DE K.

Estimation of Glycerol by the Extraction Method. WILLY LANDSBERGER (*Chem. Rev. Fett Harz Ind.*, 1905, 12, 150—152).—Compared with estimations by the acetin-method, the extraction method of Shukoff and Schestakoff (this vol., ii, 289) gives closely concordant results, especially in the estimation of glycerol in the solutions obtained by the decomposition of fats and oils by ferments. The solutions experimented with contained from 8·5 to 22 per cent. of glycerol, but good results were also obtained in the case of crude glycerols containing upwards of 80 per cent. of glycerol.

W. P. S.

Estimation of Sugar with Fehling's Solution. F. P. LAVALLE (*Ber.*, 1905, 38, 2170).—To overcome the difficulty of recognising the end-point when Fehling's solution is used to estimate sugar in solutions containing other impurities, excess of an alkali is added. The separation of cuprous oxide is prevented and the end-point sharply characterised by the disappearance of the blue colour. Five to ten c.c. of Fehling's solution are placed in a porcelain dish, 30 c.c. of aqueous sodium hydroxide (1:3) and 50—60 c.c. of distilled water added, the mixture heated to boiling, and the sugar solution then run in.

F. F. A.

[Approximate] **Estimation of Reducing Sugars and Dextrins in presence of Starch and Soluble Starch.** JULES WOLFF (*Ann. Chim. anal.*, 1905, 10, 233—235).—The liquid resulting from the maceration of 25 c.c. of a 4·5 per cent. starch paste and 5—10 c.c. of barley extract is diluted to 50 c.c., and in 10 c.c. of this the reducing sugar (maltose) is estimated as usual by the copper process. Twenty-five c.c. of the solution are then diluted to 50 c.c. with saturated barium hydroxide, which precipitates the starch whether dissolved or still in the state of paste. Twenty-five c.c. of the filtrate are then mixed with 0·25 c.c. of sulphuric acid and heated in an autoclave for 20 minutes at 120° in order to convert the dextrins and the maltose into dextrose. The liquid is diluted to 50 c.c., filtered, and treated with copper solution as usual. The total dextrose thus found represents the starch actually acted on by the barley extract in a certain time. The figures obtained also enable the amount of dextrin to be calculated. In this process, due allowance must, of course, also be made for the reducing matters contained in the barley extract.

L. DE K.

Estimation of Saccharose in presence of Lævulose and Dextrose. HENRI PELLET and L. PELLET (*Chem. Centr.*, 1905, i, 1572—1573; from *Bull. Assoc. Chim. Sucr. et Dist.*, 22, 744—752).—In reply to Dupont, the authors state that the Clerget formula with suitable modification may be safely applied in the polarimetric estimation of saccharose in cane-sugar molasses. The estimation is not affected by a slight excess of acetic or sulphurous acid.

L. DE K.

Estimation of Saccharose in presence of Dextrose and Lævulose. FRANÇOIS DUPONT (*Chem. Centr.*, 1905, i, 1573; from *Bull. Assoc. Chim. Sucr. et Dist.*, 22, 753).—The author, in reply to

Pellet and Pellet (see preceding abstract), now states that he agrees with their views. L. DE K.

Formation of Lactosazone. W. C. DE GRAAFF (*Chem. Centr.*, 1905, i, 1573; from *Pharm. Weekblad*, 42, 346—349).—1.5 mg. of the supposed lactose is boiled for two minutes with 1 drop of phenylhydrazine and 2 drops of acetic acid. Water is added until the mixture becomes turbid and it is then examined under the microscope after adding some more water to the slide. In the presence of lactose, typical globular aggregates of small, sharp, bright yellow needles of lactosazone are formed. When dealing with very small traces of lactose, the solution may be agitated with benzene and the latter allowed to evaporate. Sometimes it is necessary to recrystallise the osazone. L. DE K.

Estimation of β -Hydroxybutyric Acid in Urine. JOHN H. RYFFEL (*Proc. Physiol. Soc.*, 1905, lvi—lviii; *J. Physiol.*, 32).—The method consists in heating the urine with sodium hydroxide and ammonia to prevent frothing, adding sulphuric acid, distilling with steam, and determining the crotonic acid which passes over by saturating with bromine and estimating the excess of bromine iodometrically. W. D. H.

[Detection of] Glyoxylic Acid. HANS EPPINGER (*Beitr. chem. Physiol. Path.*, 1905, 6, 492—501. See this vol., ii, 543).

Estimation of Glycuronic Acid. BERNHARD TOLLENS (*Zeit. physiol. Chem.*, 1905, 44, 388—390. Compare Neuberg and Neimann, this vol., ii, 426; Tollens and Chalmot, *Abstr.*, 1891, 768; Mann and Tollens, 1895, ii, 335).—It is pointed out that the method previously described gives approximate results. J. J. S.

Chemical Analysis and Cryoscopy of Milk. HENRI LAJOUX (*J. Pharm. Chim.*, 1905, [vi], 21, 577—591).—The freezing point of pure milk was found to lie between -0.54° and -0.58° . For the mixed milk of many cows, the freezing point is practically constant at -0.55° , but the milk of any individual cow may give a figure as low as -0.54° . The freezing point is not affected by the feeding or breed of the animal, or by the season of the year. The addition of water to milk raises the freezing point of the latter, and the percentage quantity of added water may be calculated from the reading obtained. The amount of fat in the milk is without influence. W. P. S.

Saponification of Fat by Ammonia in the Rösé-Gottlieb Method of estimating Fat in Milk. ANTON BURR (*Milchw. Zentr.*, 1905, 1, 248—250).—The results of the experiments described in this paper show that none of the fat is saponified by the excess of ammonia used in the Rösé-Gottlieb method. Emulsions of butter fat and water, when analysed by this process, yielded the amounts of fat originally weighed out, showing that no loss of fat, due to possible

saponification, had taken place. In the case of milk, the risk of saponification is, moreover, still less, as a considerable portion of the ammonia combines with the casein. W. P. S.

New Test for Formalin in Milk. FRANZ UTZ (*Chem. Zeit.*, 1905, 29, 669).—Equal parts of milk and hydrochloric acid of sp. gr. 1.19 are heated with a few granules of vanillin. If formalin is not present, the liquid turns a beautiful violet or raspberry colour, but if traces of formalin are present the liquid turns yellow. The reaction is stated to be very delicate. L. DE K.

The Sichler "Sinacid Butyrometry." WILHELM SCHNEIDER (*Chem. Zeit.*, 1905, 29, 690).—The author having made comparative experiments with the methods of Gerber and of Sichler for the estimation of fat in milks, pronounces in favour of the former. The experiments were made both with cow's and goat's milk. L. DE K.

Oxidising Action of Impure Ether containing Peroxide, and its Influence on Kreis's Reaction. HUGO DITZ (*Chem. Zeit.*, 1905, 29, 705—710).—When a rancid specimen of cocoa-nut oil is agitated with an equal volume of concentrated hydrochloric acid and a freshly prepared solution of phloroglucinol in ether is added, Kreis's colour reaction does not take place. The reaction does take place, however, when special precaution is taken to free the ether used from any peroxide contained in it. The ethyl peroxide present in impure ether exerts a much stronger oxidising action than does the hydrogen peroxide present.

Kreis's reaction also takes place when phenols containing two hydroxyl groups in the meta-position are substituted for phloroglucinol. A. McK.

Detection of Linseed Oil in Nut Oil. GEORGES HALPHEN (*Bull. Soc. chim.*, 1905, [iii], 33, 571—572).—The test used is a special form of that already described (*Abstr.*, 1902, ii, 293). Sufficient bromine is added to 10 c.c. of carbon tetrachloride to make 15 c.c. of liquid, of which 1 c.c. is added to 0.5 c.c. of the oil, previously dissolved in 10 c.c. of ether. This mixture is then warmed at 25°, when, if linseed oil is present, a precipitate is formed in less than two minutes. A precipitate is eventually formed under these conditions with nut oil alone, but only after the lapse of at least seven minutes. The presence of poppy oil, which is sometimes added as an adulterant, does not interfere with the test. T. A. H.

Estimation of Certain Hydrazides. CONCETTO MASELLI (*Gazzetta*, 1905, 35, i, 267—273).—When aqueous solutions of salts of semicarbazide or semioxamazide are boiled with dilute acids, decomposition occurs with quantitative separation of ammonia and hydrazine, according to the equations: $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 + 2\text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2\text{H}_4$ and $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 + 2\text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2 + \text{H}\cdot\text{CO}_2\text{H} + \text{N}_2\text{H}_4$.

The quantity of semicarbazide in a solution can hence be estimated either (1) by determining the amount of hydrazine set free by adding a known volume in excess of a standard solution of potassium iodate, boiling until all the iodine separated is removed, and titrating the liquid with standard sodium thiosulphate solution to determine the excess of potassium iodate remaining in the solution, or (2) by determining the amount of ammonia set free by rendering the liquid alkaline with sodium hydroxide and distilling the ammonia into a known volume of standard acid solution. Both these methods give excellent results. With the semioxamazide, oxalic acid is formed on boiling with dilute sulphuric acid, so that in this case only the ammonia method can be used for the estimation; here also very good results are obtained.

T. H. P.

Detection of Antipyrine in Dimethylaminoantipyrine [Amidopyrine]. PAUL BOURCET (*Bull. Soc. chim.*, 1905, [iii], 33, 572—573).—An admixture of 2 per cent. or more of antipyrine with the more expensive substance amidopyrine may be detected by adding a few drops of sulphuric acid and then a small quantity of a saturated solution of sodium nitrite to a solution of from 0.01 to 0.02 gram of the suspected material in 4 to 5 c.c. of water. If antipyrine is present, a comparatively stable, intense bluish-green coloration is obtained, whereas with amidopyrine alone a fugitive bluish-violet colour is produced. The amount of antipyrine present may be approximately determined by the depth and character of the coloration.

T. A. H.

Use of Potassium Bismuth Iodide for the Estimation of Alkaloids. HERMANN THOMS (*Chem. Centr.*, 1905, i, 1341—1342; from *Ber. Deut. pharm. Ges.*, 15, 85—91).—The sulphuric acid solution of the alkaloid is precipitated with 10 c.c. of the ordinary potassium bismuth iodide reagent, and the precipitate is washed with 10 c.c. of 5 per cent. sulphuric acid. The precipitate and filter are now transferred to a wide-mouthed 200 c.c. stoppered cylinder and well shaken with a mixture of 10 grams of powdered crystallised sodium carbonate and 10 c.c. of 10 per cent. sodium hydroxide. Fifty c.c. of ether (added in 2 portions of 25 c.c.) are added, and the whole is gently shaken for 20 minutes, the cylinder being held vertically. Twenty-five c.c. of the ethereal layer are then pipetted off and titrated with $N/100$ hydrochloric acid, with iodeosin as indicator. L. DE K.

Alkaloid Reactions. Quinine and Cinchonine. C. REICHARD (*Chem. Centr.*, 1905, i, 1438—1439; from *Pharm. Zeit.*, 50, 314—315).—If a few drops of a strong solution of mercurous nitrate are evaporated on a porcelain lid and the residue mixed with a trace of quinine or cinchonine sulphate and a drop of water, reduction of mercury takes place, particularly with cinchonine. Mercuric chloride is but slightly reduced. A mixture of copper oxychloride with quinine and a little hydrochloric acid turns yellowish-red; cinchonine acts a little more slowly. A hydrochloric acid solution of basic

bismuth nitrate causes a slight yellow coloration. If a drop of strong ferric chloride is allowed to dry on a porcelain lid and the spot is covered with a little quinine or cinchonine sulphate, the addition of a drop of water will cause a dark brown mass, which turns green on adding a drop of strong sulphuric acid. When treated with ammonium persulphate and a drop of sulphuric acid, quinine gives a passing yellow colour, whilst cinchonine remains perfectly colourless. With potassium dichromate and sulphuric acid, both alkaloids give a dark, blue colour passing into bluish-green. The following reactions distinguish quinine from cinchonine. With sulphuric acid and ammonium molybdate, quinine gives a pale blue colour, gradually darkening, whilst cinchonine gives at once a dark blue colour. If these blue mixtures are warmed with a little ammonium persulphate, they both effervesce and turn deep yellow. If now to the mixture is added a little 40 per cent. formaldehyde, and then a drop of strong potassium thiocyanate, the cinchonine mixture turns a dark reddish-brown, whilst the quinine mixture is not affected.

L. DE K.

Estimation of Betaine in the Products of Sugar Factories.
VLADIMÍR STANĚK (*Zeit. Zuckerind. Böhm.*, 1905, 29, 410—417. Compare Abstr., 1904, ii, 790).—The author has applied the method for estimating betaine previously described by him (*loc. cit.*) to the products of sugar factories. These products contain purine substances, peptones, and proteids, which are all precipitated by a solution of iodine in potassium iodide solution. The betaine may, however, be separated from these by means of cupric or cuprous salts, the procedure being as follows: the material (raw sugar, syrup, molasses, &c.) is dissolved in 10 per cent. sulphuric acid solution saturated with sodium chloride, after which the potassium tri-iodide solution is added drop by drop as long as a precipitate is formed. A few grams of moist powdered iodine, obtained by precipitation of an acidified solution of iodine in potassium iodide by means of sodium nitrite, is then added and the whole thoroughly mixed. After six hours, the liquid is decanted on to a Gooch filter, the precipitate being then broken up with a glass rod and also transferred to the filter, where it is washed with saturated sodium chloride solution. The precipitate is mixed with water, and finely divided copper (precipitated from a solution containing zinc and copper sulphates by means of zinc) is added until the precipitate becomes light in colour and the odour of iodine disappears, the liquid being heated and stirred meanwhile. The solution is then boiled and sufficient cupric hydroxide (precipitated from an aqueous glycerol solution of copper sulphate by sodium hydroxide) added to give the yellow precipitate a green colour. The cooled liquid is filtered through a Gooch crucible and the residue washed ten times with cold water. The nitrogen in the precipitate, which consists mainly of cuprous iodide, is then determined by Kjeldahl's method. The nitrogen in the total filtrate, which contains the betaine, is also determined by Kjeldahl's method and is calculated as betaine; 1 c.c. of *N*/10 sulphuric acid corresponds with 0.013156 gram of crystallised betaine. This method gives good and concordant results for all the important products of the sugar factory. The betaine separated in this

manner contains small quantities of another nitrogenous substance, probably choline, and traces of an apparently nitrogen-free compound.

T. H. P.

Alkaloid Reactions. Nicotine and Coniine. II. C. REICHARD (*Chem. Centr.*, 1905, i, 1486; from *Pharm. Centr.-H.*, 46, 309—313. Compare Abstr., 1904, ii, 792 and 847).—When a drop of nicotine and then a drop of hydrochloric acid are added to finely powdered dry copper oxychloride, the mass becomes violet-blue, whilst coniine under similar conditions forms a bright green solution which gradually becomes colourless. The residue left by allowing a drop of a concentrated aqueous solution of mercurous nitrate to evaporate on a porcelain plate, when treated with coniine or nicotine, gives a deep black coloration at once in the first case, but only gradually in the second. If mercuric chloride is used instead of mercurous nitrate, both alkaloids give a very slight yellow coloration, which, on the addition of a drop of sulphuric acid, becomes faintly red when nicotine is present, but colourless when coniine is present. When coniine is added to an equal quantity of cobalt nitrate, the mixture becomes violet, whilst nicotine forms a violet-blue coloration. The residue left by allowing an aqueous solution of α -nitroso- β -naphthol to evaporate, when treated with coniine or nicotine, gives a green or a yellowish-brown coloration respectively. A solution of α -naphthol added to a drop of coniine or nicotine is colourless, but on addition of hydrochloric acid the nicotine solution turns yellow, whilst the coniine remains unchanged. An intense yellow coloration is gradually formed when hydrochloric acid is added to a mixture of bismuth subnitrate with nicotine, but coniine under similar conditions remains white. A trace of nicotine, when added to a 40 per cent. solution of formaldehyde, immediately produces a yellow coloration, and on adding a drop of concentrated sulphuric acid the colour becomes similar to that of a dilute solution of cobalt nitrate; coniine and sparteine do not give these reactions. Nicotine may also be distinguished from coniine or sparteine by the yellow coloration which is formed when the alkaloid is mixed with a few crystals of ammonium persulphate and concentrated sulphuric acid added. E. W. W.

Alkaloid Reactions (Sparteine, Coniine, Nicotine). C. REICHARD (*Chem. Centr.*, 1905, ii, 171—172; from *Pharm. Centr.*, 48, 385—388).—A series of new tests are given for *sparteine*, the most characteristic of which are as follows: sodium picrate gives a yellow with sparteine and coniine but a reddish-yellow with nicotine. On adding sulphuric acid, the nicotine mixture turns yellow. If to the three mixtures is now added a little ammonium persulphate and a drop of strong potassium thiocyanate, the sparteine assumes a fine orange-red colour, while the others are not affected. On evaporating a mixture of ferric chloride and potassium thiocyanate and then moistening the spot with water containing sparteine, the mixture turns a beautiful bluish-violet; nicotine and coniine give a green colour.

New tests are also given for *coniine* and *nicotine*, of which the following are the most characteristic. Nicotine gives a yellowish-green with ammonium molybdate; coniine and sparteine are not affected. If

nicotine is added to a mixture of ammonium molybdate and sulphuric acid the mixture also turns a yellowish-green which, on adding ammonium persulphate, becomes a beautiful purplish-violet, gradually changing to dark yellow. Coniine and sparteine give a faint blue colour which turns dark yellow with persulphate.

When nicotine is added to powdered potassium ethyl sulphate moistened with sulphuric acid, the mass turns first yellow and then red; coniine and sparteine give no reaction.

L. DE K.

Estimation of Lecithin in Grape Stones and in Wine. F. MURARO (*Gazzetta*, 1905, 35, i, 314—319).—The author's experiments show that absolute alcohol extracts lecithin from grape stones more completely at 80° than at 50°, but that with wines the maximum amount of lecithin is extracted at 50°, the quantity obtained at 80° being, however, greater than that yielded by neutralised wine at the same temperature.

It is probable that the conclusions of Weirich and Ortlieb (*Abstr.*, 1904, ii, 304) are incorrect and that pasteurised wines still contain lecithin.

T. H. P.

Malt Analysis. II. Estimation of Moisture and Extract. JOHN SIMPSON FORD and JOHN M. GUTHRIE (*Journ. Inst. Brewing*, 1905, 11, 326—344).—The ordinary method of estimating the moisture of malt, by drying in a steam-oven or in an air-oven at 105°, gives results which are both erroneous and inconsistent, since many malts gain in weight owing to oxidation by the air. Perhaps the most satisfactory results are arrived at by drying the malt at 110° in a current of hydrogen, absorbing the expelled water by means of sulphuric acid or phosphoric oxide, and checking the result by noting the loss in weight of the malt; the figures are in general identical. The use of vacuum drying appliances at 105—110° would undoubtedly yield results approximate to the truth, but such appliances are expensive and troublesome; where, however, a correct value is required, as in the determination of extract by the "proportionality" or "known weight" method, they should be employed. For uniformity of result, all that is required is the use of an inert gas, preferably carbon dioxide, in conjunction with the ordinary water-oven, the values thus obtained being concordant, although probably lower than the real values. The authors describe a suitable carbon dioxide generator and reservoir connected with a steam-oven.

The authors discuss the different methods in use for the estimation of the "extract" of malts, and conclude that the most convenient is that given by Heron. They find, however, that 10 c.c. is a more exact average volume of the grains obtained from 50 grams of malt than 15 c.c., as stated by Heron.

T. H. P.

General and Physical Chemistry.

Emission of Light from the Vapours of Alkali Metals and their Salts, and the Centres of this Emission. PHILIPP LENARD (*Ann. Physik*, 1905, [iv], 17, 197—247).—The experimental part of this paper deals with the coloured glow exhibited by fused salts of the alkali metals. The glow in the case of caesium and rubidium is yellowish-green, in the case of potassium green, in the case of sodium bright blue, in the case of lithium duller blue. These glow colours are attributed to the metallic cation. The continuous ground visible in flame spectra of salts of the alkali metals is probably emitted also by the metallic cations.

The paper contains many other detailed observations and theoretical propositions, for which the original must be consulted. J. C. P.

Limits of Visibility of Fluorescence and the Maximum Value of the Absolute Weight of the Atom of Hydrogen. WALTHER SPRING (*Bull. Acad. roy. Belg.*, 1905, 201—211).—A solution of fluorescein in optically pure water was subjected to the action of a powerful beam of electric light, and the limit of dilution was observed at which a visible green fluorescence was produced. Assuming under these conditions that one cubic millimetre of the solution contained one molecule of fluorescein ($C_{20}H_{10}O_5K_2=408$), the value 2.5×10^{-21} grams is obtained for the superior limit of the weight of the atom of hydrogen, which is one-twenty-thousand-millionth part of the value 5×10^{-11} calculated by Annaheim (this Journal, 1877, i, 31), but is about seven thousand times as great as the value 3.45×10^{-25} calculated from the kinetic theory of gases. P. H.

Photochemical Action of Mercuric Oxalate (Eder's Solution) in Absence of Oxygen and in Presence of Fluorescent Compounds. A. JODLBAUER and HERMANN VON TAPPEINER (*Ber.*, 1905, 38, 2602—2609. Compare Abstr., 1904, i, 131; Gros, *ibid.*, 1901, ii, 433).—Numerous investigators have shown previously that processes of oxidation, for example, of hydriodic acid, fluorescein, potassium iodide, silver, arsenious acid, benzyl alcohol, and salicylaldehyde are accelerated by the presence of a fluorescent substance such as acridine, quinine, erythrosin, &c.

Experiments are now described which prove that processes other than oxidations, for example, the photochemical decomposition of Eder's solution (Roloff, Abstr., 1894, ii, 221), are accelerated by the presence of fluorescent substances such as fluorescein, its chloro-, bromo-, and iodo-derivatives, dichloro-anthracene- and anthraquinone-disulphonic acids, acridine, benzoflavine, phenyl-2-methylquinoline, quinine, and probably æsculin. The following, however, had no accelerating effect: phenosafranine, fluorindindisulphonic acid, methylene-blue, harmalin, and also the following: tetranitrofluorescein, alizarin-blue hydrogen sulphite, and ethyl-red, which are without appreciable fluorescence.

It is also shown that the photochemical decomposition of Eder's solution proceeds more readily in a vacuum or in the presence of carbon dioxide or hydrogen than in the presence of oxygen.

J. J. S.

Relations between Power of Absorption of Radiant Energy and Chemical Character. ALFRED BYK (*Chem. Centr.*, 1905, ii, 6—7; from *Physikal. Zeit.*, 6, 349—353).—The original paper contains a comprehensive account of the relationship between the power of absorption of radiant energy and chemical and physical properties. In organic compounds, the OH and NH₂ groups appear even in the ultra-violet spectrum to play the part of an auxochrome, and the chromophoric character of double linkings is also apparent in this portion of the spectrum. The constitution of inorganic compounds is of less importance in optical phenomena. Increase of molecular weight of either organic or inorganic compounds has usually a bathochromic effect. The relations between atomic weight and spectra, and between electrical conductivity and non-selective absorption are also discussed.

E. W. W.

Fundamental Principles of Three-colour Photography. J. PRECHT and ERICH STENGER (*Chem. Centr.*, 1905, ii, 7; from *Physikal. Zeit.*, 6, 329—331).—The abstract contains a description of the theory of the three-colour photographic process which is mainly of a physical character. The energy required for the decomposition of silver bromide is conveyed by means of the dye, the chemical process being the same in the case of all the three colours, the dyes merely affecting the time of exposure. The eye can distinguish differences of shade up to 660 μ , but the sensitiveness of the silver bromide plate decreases with enormous rapidity beyond 660 μ . A dye is therefore required which has a maximum of sensitiveness at about 650 μ .

E. W. W.

Energy of Chemical Radiation through Three-colour Filters. J. PRECHT and ERICH STENGER (*Chem. Centr.*, 1905, ii, 7—8; from *Physikal. Zeit.* 6, 332—334. Compare preceding abstract).—The density of a plate is proportional to the quantity of reduced silver, which is again proportional to the energy used in chemical action. The proportion of the latter to the whole energy radiated to the plate has been measured for the three-colour filters by physical methods which are described.

E. W. W.

Radiation-sensitiveness of Silver Bromide Gelatin for White, Green, and Orange Light. J. PRECHT and ERICH STENGER (*Chem. Centr.*, 1905, ii, 8; from *Physikal. Zeit.*, 6, 334—336. Compare preceding abstracts).—The relation between the energy received by radiation and the density of silver precipitates in ordinary silver bromide plates has been determined for white, green, and orange light. For the same density, the energy is about 250 times as great in green light as in white. For green and orange light, the relation is nearly the same for normal densities. When a quantity of energy

sufficient to produce a certain density is first imparted to the layer, then the gradation in the case of ordinary undyed silver bromide is very nearly the same for the same quantity of energy when white, green, or red light is employed for illumination. E. W. W.

Effect of High Temperatures on the Rate of Decay of the Active Deposit from Radium. HOWARD L. BRONSON (*Amer. J. Sci.*, 1905, [iv], 20, 60—64. Compare Curie and Danne, *Abstr.*, 1904, ii, 306).—Temperatures between 700° and 1100° have very little, if any, effect on the rate of decay of the active deposit from radium. It may be assumed that radium *C* has the shorter rather than the longer of the two periods, and that radium *B* is the more volatile. The author's experiments indicate that 28 minutes and 21 minutes are too long for the decay periods of radium *B* and radium *C*, and that 26 minutes and 19 minutes are more nearly correct. J. C. P.

New Radiation produced in Atmospheric Air by the Rays from Radiotellurium. B. WALTER (*Ann. Physik*, 1905, [iv], 17, 367—374).—The author's experiments indicate the production in atmospheric air in contact with radiotellurium of a radiation with properties resembling those of ultra-violet light. The constituent of the atmosphere which is thus affected is pre-eminently the nitrogen. When other gases, such as carbon dioxide, nitrous oxide, coal gas, oxygen, and hydrogen, are in contact with the radiotellurium, the effect in question is very small. J. C. P.

Radioactivation by means of Uranium. HENRI BECQUEREL (*Compt. rend.*, 1905, 141, 87—90).—As has been shown previously, uranium *X* is precipitated, along with barium sulphate, from a solution of uranium chloride on addition of barium chloride and sulphuric acid. In the same manner, if water which has been exposed to radium emanation is treated with barium chloride and sulphuric acid, the barium sulphate obtained is radioactive, the rate of decay of the activity approximating to that of radium emanation, and the solution from which the emanation has been removed is inactive. It has been found possible to precipitate uranium *X* together with radium emanation: one-half of a solution of uranium chloride was exposed to radium emanation for some days, and both halves of the solution treated in the same manner with barium chloride and sulphuric acid. The barium sulphate from the solution which had been exposed to radium emanation was found 80 minutes after precipitation to be seven times as active as the sulphate from the unexposed solution. The excess of activity diminished at the rate of decay of radium emanation, and at the end of one day the activity of the barium sulphate from the exposed solution had diminished to slightly less than the activity of the sulphate from the standard. After the first day, the rate of decay, being due to uranium *X*, was the same for both sulphates.

The activity of uranium *X* which has been precipitated together with barium sulphate is not diminished when the sulphate is heated to bright redness in the oxyhydrogen blowpipe flame.

Uranium *X* is removed from uranium chloride solutions by boiling

with lampblack which has been washed with alcohol and ether. The precipitate from 5 grams of uranium chloride had an activity $1/9$ of that of 1.32 grams of the black oxide of uranium. On igniting the active lampblack in a current of oxygen in a platinum crucible, a residue of inappreciable weight was obtained consisting of small fused grains which contained uranium, and had an activity six times that of the uncalcined lampblack. In eight days, the activity of the residue had increased to that of 1.32 grams of the black oxide of uranium.

In a similar experiment with 4 grams of lampblack and 150 grams of uranium chloride, the lampblack acquired an activity equal to half that of the standard black oxide. After ignition, the residue was treated with hydrochloric acid, and the undissolved substance, as well as the residue obtained on evaporation of the acid solution, was found to have an activity equal to that of the uncalcined lampblack.

Uranium chloride which has been boiled with lampblack is not capable of rendering a second sample active. If the active lampblack is thoroughly washed with cold dilute hydrochloric acid, the residue is only very slightly active. The inactive lampblack leaves no residue on ignition, the activity is therefore due to the precipitation of a solid, highly radioactive substance. G. Y.

Relative Proportion of Radium and Uranium in Radioactive Minerals. ERNEST RUTHERFORD and BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1905, [iv], 20, 55—56. Compare Boltwood, this vol., ii, 295).—Comparative experiments on the activity of radium bromide and of a very pure sample of uraninite containing 74—75 per cent. of uranium lead to the conclusion that the quantity of radium associated with one gram of uranium in a radioactive mineral is approximately 7.4×10^{-7} gram. J. C. P.

Radioactive Constituents of Wiesbaden Thermal Springs. FERDINAND HENRICH and GÜNTHER BUGGE (*Zeit. angew. Chem.*, 1905, 18, 1011—1014. Compare this vol., ii, 6).—The deposit from the pipes of the Wiesbaden thermal springs, formerly examined, consisted mainly of aragonite and was radioactive, remaining so when heated at 110° for several hours. The gas evolved on the addition of hydrochloric acid was also radioactive. The deposit was separated into several fractions, and the radioactivity of each fraction examined. The radioactivity of the gas evolved from the Adler spring and of the water itself is due to radium emanation. A. McK.

Mercury Arc Lamp with Quartz Jacket suitable for Chemical Purposes. FRANZ FISCHER (*Ber.*, 1905, 38, 2630—2633).—This lamp consists of an exhausted double-walled quartz cylinder fixed with sealing-wax into the neck of a surrounding cylindrical glass vessel, which is connected with an air-pump. The anode consists of an iron ring, which surrounds the quartz cylinder and is suspended by means of two platinum wires fused into the walls of the glass vessel. Mercury is placed in the bottom of the latter to serve as cathode. Near the bottom of the glass vessel is an outer ring of tin foil connected with a copper wire so that an induction coil may be used

for lighting. The glass vessel dips into a small mercury trough into which the current is led.

Arrangements are made to cool the lamp both internally and externally, so that the temperature in the interior of the lamp is kept down, thus maintaining a low density of the mercury vapour, and favouring the formation of ultra-violet light. Figures of the lamp and accessory apparatus are given in the original. T. H. P.

Concentration Cells in Liquid Ammonia. HAMILTON P. CADY (*J. Physical Chem.*, 1905, 9, 477—503).—Concentration cells of the type sodium amalgam | sodium nitrate solution (c_1) | sodium nitrate solution (c_2) | sodium amalgam were constructed with liquid ammonia as solvent, the method of preparation being fully described. For this cell and a similar cell with sodium chloride, the *E.M.F.* was determined and compared with that given by the expression $E = 0.000198T \log c_1/c_2$. The observed values are in most cases about 80 to 90 per cent. of those calculated, this difference being ascribable to the incomplete dissociation. Better agreement was obtained by the use of the formula $E = 0.000198T \log R_2/R_1$, the ionic concentrations being inversely proportional to the resistances. Although the agreement is only approximate, it shows clearly the validity of a logarithmic expression, and that the laws for aqueous solution apply also to ammonia solution. Some cells with bivalent ions and sodium chloride cells without diffusion were also examined, accord with the estimated values being in these cases also fairly approximate. The *E.M.F.* of a cell having different amalgams as electrodes was also determined and found to be 1.42 times the calculated value; the similar ratio for a cell with pyridine as solvent is 1.41. The *E.M.F.* of three oxidation and reduction cells was also determined.

L. M. J.

Iodine Titration Voltameter. DAVID A. KREIDER (*Amer. J. Sci.*, 1905, [iv], 20, 1—10).—A new voltameter containing a strong solution of potassium iodide covered with a layer of dilute hydrochloric acid. On passing the current, iodine is liberated, the amount of which may be titrated, this being dependent on the strength of the current.

For further particulars the original article and illustrations should be consulted.

L. DE K.

Cause of the Spontaneous Depression of the Cathode Potential in the Electrolysis of Dilute Sulphuric Acid. JULIUS TAFEL and BRUNO EMMERT (*Zeit. physikal. Chem.*, 1905, 52, 349—373).—In continuation of previous work (Tafel, this vol., ii, 223) it is shown that when dilute sulphuric acid is electrolysed with a platinum anode, the current density at that electrode being comparatively low, chemically recognisable quantities of platinum are dissolved. These small quantities of platinum suffice to account for the depressions of the cathode potential previously observed, the sensitiveness of different cathode metals varying considerably. In

the case of a silver cathode, 0.0001 mg. of platinum is able to produce the depression of the potential for a cathode surface of 10 sq. cm. The effect is produced by the precipitation of the platinum on the cathode, but even then it may remain latent. The action of the platinum is apparently not to convert the cathode into a platinum cathode, but to assist catalytically some chemical change of the cathode surface. The action of gold on the cathode potential of other metals is insignificant compared with that of platinum. J. C. P.

Electrolytic Potential of Chromous Salts (Electrochemical Equilibrium between Various Degrees of Oxidation). II. ARBIGO MAZZUCHELLI (*Gazzetta*, 1905, 35, i, 417—448. Compare Abstr., 1902, ii, 119).—In investigating the conversion of chromic into chromous ions and *vice versa*, the author uses tin electrodes in mixtures of chromic and chromous chlorides, sulphates, fluorides, and acetates. Copper and mercury electrodes give varying results, and with these metals and also with tin higher potentials are obtained than with platinum. All the determinations were made in a stream of carbon dioxide. With two similar tin electrodes, differences up to 0.06 volt were obtained. On adding fresh chromic or chromous salt, the *E.M.F.* sometimes changes in the wrong direction at first, but afterwards assumes the normal value determined by the equation $E = K - A \log(C^{III}/C^{II})$. Similar irregularities are observed with platinum in hydrogen peroxide solution, but in this case the platinum acts catalytically, whilst tin has only a very small catalytic influence on chromous salts. For a mixture of chromic and chromous chlorides or acetates at 17—18°, with a normal Hg_2SO_4 electrode, the constant *K* of the electrochemical equilibrium is 1.04—1.06 volts, whilst for the fluorides it has the value 1.17—1.19 volts. With the sulphates, less concordant values are obtained for the different solutions and electrodes, but the most probable value for *K* is 0.98—1.03 volts.

The following table gives the oxidation potentials of chromous-chromic salts and also those of ferrous-ferric salts, the values all being referred to the normal hydrogen electrode :

	Chlorides.	Sulphates.	Fluorides.	Acetates.
Iron	-0.705	-0.657	about -0.270	—
Chromium ...	+0.38	about +0.33	+0.51	+0.38

T. H. P.

Boiling Points of Ammonia, Methylamine, Methyl Chloride, and Sulphur Dioxide. HARRY D. GIBBS (*J. Amer. Chem. Soc.*, 1905, 27, 851—865).—A *résumé* is given of previous work on this subject, together with a criticism of the methods employed and the results obtained. An improved apparatus has been devised for the determination of these boiling points, and is described with the aid of a diagram. Special methods were employed for purifying the liquids. The boiling points of ammonia, methyl chloride, and sulphur dioxide were found to be -33.46°, -24.09°, and -10.09° respectively under 760 mm., whilst that of methylamine was found to be -6.7° under 755.67 mm. pressure. E. G.

Determination of Molecular Weight by Use of Solvents with High Boiling Points. LEOPOLD RÜGHEIMER [with S. TOECHE MITTLER and E. RUDOLFI] (*Annalen*, 1905, **339**, 297—310).—Instead of using the Beckmann method of determining molecular weights by the raising of the boiling point, it is found advisable to employ the lowering of vapour pressure, a method which can be adapted to solvents with boiling points above that of mercury. At the same time, the measurements can be made at any chosen pressures, and also at different temperatures. An exact description of the apparatus, the air-thermometers, and manometers, and of the method of using them is given in the paper.

K. J. P. O.

Relation between the Logarithmic Temperature Constant and Heat Evolution. JOH. PLOTNIKOFF (*Zeit. Elektrochem.*, 1905, **11**, 389—390. Compare this vol., ii, 376).—Since $d\log K/dT = q/RT^2 = \beta$, it follows that $q = \beta RT^2$. Examples of the calculation of q are given, but the results are not compared with experimental values.

FRIEDRICH AUERBACH (*Zeit. Elektrochem.*, 1905, **11**, 433—434) points out several errors in the above paper which are admitted by JOH. PLOTNIKOFF in a later communication (*ibid.*, 1905, **11**, 434); the latter therefore withdraws the paper, with the exception of the above result.

T. E.

Numerical Results of a Systematic Investigation of the Heats of Combustion and Formation of Volatile Organic Compounds. JULIUS THOMSEN (*Zeit. physikal. Chem.*, 1905, **52**, 343—348).—In the following list the heats of combustion given are subject to the condition that the products of combustion are gaseous carbon dioxide, nitrogen, sulphur dioxide, and chlorine, bromine, and iodine in the form of vapour and liquid water. The numbers given under p are heats of formation from amorphous carbon, rhombic sulphur, molecular gaseous hydrogen, nitrogen, chlorine, bromine, and iodine; the method of calculation and the fundamental figures used will be evident from the example of ethane, for which $p = 2 \times 96.96 + 3 \times 67.49 - (370.44 - 5 \times 0.29) = 27.40$ Cal. The numbers given under p are referred to by the author as “empirical” heats of formation, because they refer to a special condition of carbon. In the column marked P , the values given are heats of formation from carbon atoms, &c.; these values are termed “absolute” heats of formation, and the relation between the values in the two columns is given by the equation $P = p + a.38.38$, where a is the number of carbon atoms in a molecule of the compound. Relationships between heat of formation and constitution are much more easily recognised from the “absolute” heats of formation than from the “empirical” heats of formation.

Substance.	Formula.	Heat of combustion at constant pressure.	Heat of or mation at constant volume.	
			<i>p.</i>	<i>P.</i>
<i>Hydrocarbons.</i>				
Methane	CH ₄	211·93	21·17	59·55
Ethane	C ₂ H ₆	370·44	27·40	104·16
Propane	C ₃ H ₈	529·21	33·37	148·51
Trimethylmethane	CH(CH ₃) ₃	687·19	40·13	193·65
Tetramethylmethane	C(CH ₃) ₄	847·11	44·95	236·85
Diisopropyl	(C ₃ H ₇) ₂	999·20	57·60	287·88
Benzene	C ₆ H ₆	799·35	- 13·67	216·61
Toluene	C ₇ H ₈	955·68	- 5·26	263·40
Mesitylene	C ₉ H ₁₂	1282·31	- 2·41	343·01
Pseudo-cumene	C ₉ H ₁₂	1281·51	- 1·59	343·83
Ethylene	C ₂ H ₄	333·25	- 3·29	73·47
Propylene.....	C ₃ H ₆	492·74	+ 2·06	117·20
Trimethylene	C ₃ H ₆	499·43	- 4·63	110·51
<i>iso</i> Butylene	C ₄ H ₈	650·62	+ 8·92	162·44
<i>iso</i> Amylene	C ₅ H ₁₀	807·63	+ 16·65	208·55
Diallyl	C ₆ H ₁₀	932·82	- 11·58	218·70
Acetylene.....	C ₂ H ₂	310·05	- 47·77	28·99
Allylene	C ₃ H ₄	467·55	- 40·53	74·61
Dipropargyl.....	C ₆ H ₆	882·88	- 97·20	133·08

Halogen Compounds.

Methyl chloride	CH_3Cl	176·95	21·97	60·35
Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	334·11	29·55	106·31
Propyl chloride	$\text{C}_3\text{H}_7\text{Cl}$	492·33	36·02	151·16
isoButyl chloride.....	$\text{C}_4\text{H}_9\text{Cl}$	650·09	43·05	196·57
Monochloroethylene	$\text{C}_2\text{H}_3\text{Cl}$	298·34	- 2·46	74·30
Monochloropropylene.....	$\text{C}_3\text{H}_5\text{Cl}$	453·37	+ 7·25	122·39
Allyl chloride	$\text{C}_3\text{H}_5\text{Cl}$	454·68	+ 5·94	121·08
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	763·88	- 12·38	217·90
Ethylene chloride	$\text{C}_2\text{H}_4\text{Cl}_2$	296·36	+ 33·12	109·88
Ethylidene chloride	$\text{C}_2\text{H}_4\text{Cl}_2$	296·41	33·07	109·83
Chloroacetol.....	$\text{C}_3\text{H}_6\text{Cl}_2$	453·88	40·34	155·48
Carbonyl chloride	COCl_2	41·82	54·85	93·23
Chloroform	CHCl_3	107·03	23·53	61·91
Monochloroethylene chloride...	$\text{C}_2\text{H}_3\text{Cl}_3$	262·48	32·82	109·58
Tetrachloromethane	CCl_4	75·93	20·45	58·83
Tetrachloroethylene	C_2Cl_4	195·07	- 1·73	75·03
Methyl bromide	CH_3Br	184·71	+ 14·21	52·59
Ethyl bromide	$\text{C}_2\text{H}_5\text{Br}$	341·82	21·84	98·60
Propyl bromide	$\text{C}_3\text{H}_7\text{Br}$	499·29	29·11	144·25
Allyl bromide	$\text{C}_3\text{H}_5\text{Br}$	462·12	- 1·50	113·64
Methyl iodide	CH_3I	196·08	2·84	41·22
Ethyl iodide.....	$\text{C}_2\text{H}_5\text{I}$	353·73	9·93	86·69

Ethers, &c.

Ethylene oxide	$(\text{CH}_2)_2\text{O}$	312·55	17·22	93·98
Methyl ether	$(\text{CH}_3)_2\text{O}$	349·36	48·19	124·95
Methyl ethyl ether.....	$\text{CH}_3\cdot\text{O}\cdot\text{C}_2\text{H}_5$	505·87	56·42	171·56
Ethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$	659·60	67·43	220·95
Methyl allyl ether	$\text{CH}_3\cdot\text{O}\cdot\text{C}_3\text{H}_5$	627·20	32·05	185·57
Allyl ether	$(\text{C}_3\text{H}_5)_2\text{O}$	911·10	9·85	240·13

Substance.	Formula.	Heat of combustion at constant pressure.	Heat of formation at constant volume.	
			<i>p.</i>	<i>P.</i>
<i>Ethers, &c. (continued).</i>				
Methyl propargyl ether..	$\text{CH}_3 \cdot \text{O} \cdot \text{C}_3\text{H}_3$	603·83	- 12·36	141·16
Anisole	$\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_5$	936·30	+ 13·83	282·49
Methylal	$\text{CH}_2(\text{O} \cdot \text{CH})_{3/2}$	476·08	85·92	201·06
Trimethyl methenyl ether	$\text{CH}(\text{O} \cdot \text{CH}_3)_3$	599·18	127·27	280·79

Alcohols.

Methyl alcohol	$\text{CH}_3 \cdot \text{OH}$	182·23	50·58	88·96
Ethyl alcohol	$\text{C}_2\text{H}_5 \cdot \text{OH}$	340·53	57·02	133·78
Propyl alcohol... ..	$\text{C}_3\text{H}_7 \cdot \text{OH}$	498·63	63·66	178·80
<i>iso</i> Propyl alcohol	$\text{C}_3\text{H}_7 \cdot \text{OH}$	493·32	68·97	184·11
<i>iso</i> Butyl alcohol	$\text{C}_4\text{H}_9 \cdot \text{OH}$	658·49	68·54	222·06
Trimethylcarbinol	$\text{C}_4\text{H}_9 \cdot \text{OH}$	641·34	85·69	239·21
<i>iso</i> Amyl alcohol	$\text{C}_5\text{H}_{11} \cdot \text{OH}$	820·07	71·70	263·60
Dimethylethylcarbinol	$\text{C}_5\text{H}_{11} \cdot \text{OH}$	810·45	81·32	273·22
Allyl alcohol	$\text{C}_3\text{H}_5 \cdot \text{OH}$	464·76	29·75	144·89
Propargyl alcohol	$\text{C}_3\text{H}_3 \cdot \text{OH}$	431·10	- 4·37	110·77
Phenol	$\text{C}_6\text{H}_5 \cdot \text{OH}$	768·76	+ 16·63	246·91
Ethylene glycol	$\text{C}_2\text{H}_4(\text{OH})_2$	298·11	99·15	175·91

Aldehydes and Ketones.

Acetaldehyde	$\text{CH}_3 \cdot \text{CHO}$	281·90	47·87	124·63
Propaldehyde	$\text{C}_2\text{H}_5 \cdot \text{CHO}$	440·72	53·79	168·93
<i>iso</i> Butaldehyde	$\text{C}_4\text{H}_7 \cdot \text{CHO}$	599·90	59·31	212·83
Dimethyl ketone... ..	$(\text{CH}_3)_2 \cdot \text{CO}$	437·25	57·26	172·40
Methyl propyl ketone	$\text{CH}_3 \cdot \text{CO} \cdot \text{C}_3\text{H}_7$	754·19	69·40	251·30

Acids and Anhydrides.

Formic acid	$\text{H} \cdot \text{CO}_2\text{H}$	69·39	95·35	133·73
Acetic acid	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	225·35	104·13	180·89
Propionic acid	$\text{C}_2\text{H}_5 \cdot \text{CO}_2\text{H}$	386·51	107·71	222·85
Acetic anhydride.....	$(\text{C}_2\text{H}_3\text{O})_2\text{O}$	460·07	130·82	284·34

Esters.

Methyl formate	$\text{H} \cdot \text{CO}_2\text{CH}_3$	241·21	88·27	165·03
Methyl acetate.....	$\text{CH}_3 \cdot \text{CO}_2\text{CH}_3$	399·24	94·98	210·12
Ethyl formate	$\text{H} \cdot \text{CO}_2\text{C}_2\text{H}_5$	400·06	94·16	209·30
Methyl propionate	$\text{C}_2\text{H}_5 \cdot \text{CO}_2\text{CH}_3$	553·95	105·01	258·53
Ethyl acetate	$\text{CH}_3 \cdot \text{CO}_2\text{C}_2\text{H}_5$	546·57	112·39	265·91
Propyl formate	$\text{H} \cdot \text{CO}_2\text{C}_3\text{H}_7$	558·80	100·16	253·68
Methyl <i>isobutyrate</i>	$\text{C}_3\text{H}_7 \cdot \text{CO}_2\text{CH}_3$	716·94	106·76	298·66
<i>iso</i> Butyl formate	$\text{H} \cdot \text{CO}_2\text{C}_4\text{H}_9$	719·90	103·80	295·70
Allyl formate	$\text{H} \cdot \text{CO}_2\text{C}_3\text{H}_5$	527·90	63·28	216·80
Dimethyl carbonate	$(\text{CH}_3)_2\text{CO}_3$	357·57	136·36	251·50
Diethyl carbonate	$(\text{C}_2\text{H}_5)_2\text{CO}_3$	674·10	149·31	341·21
Ethyl nitrate	$\text{C}_2\text{H}_5 \cdot \text{NO}_3$	324·04	38·75	115·51

Substance.	Formula.	Heat of combustion at constant pressure.	Heat of formation at constant volume.	
			<i>p.</i>	<i>P.</i>
<i>Sulphur Compounds.</i>				
Hydrogen sulphide.....	H ₂ S	136·71	2·73	2·73
Methyl mercaptan	CH ₃ ·SH	298·81	5·37	43·75
Ethyl mercaptan	C ₂ H ₅ ·SH	455·65	13·27	90·03
Dimethyl sulphide	(CH ₃) ₂ S	457·35	11·57	88·33
Diethyl sulphide..	(C ₂ H ₅) ₂ S	772·17	26·23	179·75
Methyl thiocyanate.....	CH ₃ ·S·NC	398·95	-31·99	44·77
Methyl thiocarbimide.....	CH ₃ ·N·CS	392·06	-25·10	51·66
Allyl thiocarbimide.....	C ₃ H ₅ ·N·CS	675·36	-46·70	106·82
Thiophen	C ₄ H ₄ S	610·64	-15·58	137·94
Carbon disulphide	CS ₂	265·13	-25·43	12·95
Carbon oxydisulphide	COS	131·01	+37·32	75·70

Hydrogen Cyanide and Nitriles.

Cyanogen	C ₂ N ₂	259·62	-65·70	11·06
Hydrogen cyanide	HCN	158·62	-27·48	10·90
Acetonitrile	CH ₃ ·CN	312·14	-16·26	60·50
Propionitrile.....	C ₂ H ₅ ·CN	471·45	-10·83	104·31

Amines.

Ammonia	NH ₃	90·65	11·31	11·31
Methylamine	CH ₃ ·NH ₂	258·32	8·38	46·76
Dimethylamine	(CH ₃) ₂ NH	420·46	10·98	87·74
Trimethylamine	(CH ₃) ₃ N	582·63	13·55	128·69
Ethylamine	C ₂ H ₅ ·NH ₂	415·67	15·77	92·53
Diethylamine	(C ₂ H ₅) ₂ NH	734·50	26·42	179·94
Triethylamine	(C ₂ H ₅) ₃ N	1052·38	38·02	268·30
Propylamine	C ₃ H ₇ ·NH ₂	575·74	20·42	135·56
<i>iso</i> Butylamine	C ₄ H ₉ ·NH ₂	725·36	35·56	189·08
Amylamine	C ₅ H ₁₁ ·NH ₂	890·58	35·08	226·98
Allylamine	C ₃ H ₅ ·NH ₂	531·28	-2·88	112·26
Aniline	C ₆ H ₅ ·NH ₂	838·47	-19·19	211·09
Pyridine	C ₅ H ₅ N	675·07	-20·53	171·37
Piperidine	C ₅ H ₉ ·NH ₂	833·79	+24·09	215·99

Nitro-compounds and Nitrites.

Nitromethane	CH ₃ ·NO ₂	180·90	17·44	55·82
Nitroethane	C ₂ H ₅ ·NO ₂	337·94	25·14	101·90
Ethyl nitrite	C ₂ H ₅ ·O·NO	334·21	28·87	105·63
Amyl nitrite	C ₅ H ₁₁ ·O·NO	812·64	44·66	236·56
Ethyl nitrate ..	C ₂ H ₅ ·O·NO ₂	324·04	38·75	115·51

J. C. P.

Contraction exhibited by Certain Substances on Ignition.
 RICHARD LUCAS (*Zeit. physikal. Chem.*, 1905, 52, 327—342).—The contraction exhibited by cobalt oxide, magnesia, kaolin, and zirconium oxide when heated to temperatures from 100° to 2000° has been studied. The substances named were made plastic with a little water or adhesive material, and used in the form of thin rods. It is found that the

more rapidly the temperature is raised the more marked is the contraction, although when the final temperature is very high the rate at which the temperature is raised is without effect. The contraction increases rapidly with the temperature to which the rods are exposed, and approaches an end value asymptotically. The relation between the extent of contraction and the time of ignition at a given temperature is expressible by a logarithmic formula, but for very high temperatures the influence of the time vanishes. For a rod placed in the furnace in a horizontal position, the linear contraction is greater in the vertical than in the horizontal direction, and the difference increases with rising temperature of ignition. The foregoing behaviour indicates the amorphous character of the substances used. The strength of the ignited rods rises rapidly with the temperature to which they have been exposed, and approaches an end value asymptotically. Contraction and porosity are intimately connected, and the result of heating is to diminish the volume of the hollow spaces within the porous substance; the contraction is brought about probably by capillary forces, heat diminishing the viscosity of the substances, and thereby diminishing their resistance to these forces. J. C. P.

Osmotic Pressure and Freezing Points of Solutions of Sucrose. HARMON N. MORSE and JOSEPH C. W. FRAZER (*Amer. Chem. J.*, 1905, **34**, 1—99. Compare Abstr., 1902, ii, 553).—In continuing the work on the direct determination of osmotic pressure, it was found that suitable porous cells could not be obtained from the potteries, and it was therefore necessary to prepare them in the laboratory. A microscopic study has been made of thin sections of the walls of cells which had been tested previously with membranes in order to discover the peculiarities of texture which determine the suitability of a porous wall for this work. The essential qualities having been thus discovered, methods have been devised for the production of satisfactory cells.

A detailed account is given of the construction and calibration of the manometer used in determinations of osmotic pressure, and the various steps in the process of preparing the cell for use, including the deposition of the membrane. For particulars, the description and diagrams in the original must be consulted.

Considerable difficulty has been experienced owing to the temporary fluctuations of pressure resulting from changes of temperature, caused by the expansion or contraction of the liquids in the cell. In order to reduce these so-called "thermometer effects" as far as possible, the cell was placed in a specially devised box with double walls, the space between which was packed with hair felt.

A second source of error was encountered in the uncertainty regarding the true volume of that portion of the manometer, the form of which is affected by the sealing of the instrument; although this does not seriously affect the measurement of the pressure of dilute solutions, it becomes of considerable importance in the case of concentrated solutions.

A third difficulty is caused by the inversion of some of the sucrose in the cell. The amount of this inversion was determined by means

of Fehling's solution, but it is considered that the results thus obtained were below the actual quantity inverted, and it has therefore been decided to measure the inversion by means of the polariscope in future experiments.

Determinations have been made of the osmotic pressure of solutions of sucrose of various concentrations between 0.05 and 1.00 weight-normal, and from the results the molecular weight has been calculated by means of the formula $M = W(22.488 + 0.0824t)/P$, where P is the osmotic pressure at the temperature t of a weight W of the substance dissolved in 1000 grams of water. The molecular weights thus found vary between 327.9 and 347.7 and have an average value 341.2.

The results obtained in these experiments lead to the conclusion that sucrose dissolved in water exerts an osmotic pressure equal to that which it would exert if it were in the gaseous state at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.

Since the volume relations of solvent and solution play such an important part in the osmotic pressure of sucrose solutions, it was considered probable that the so-called abnormal freezing points at the higher concentrations may be dependent on, or related to, the degree of the distension of the solvent by the dissolved substance. The freezing points and density at 0°, or slightly below, at the various concentrations were therefore determined. From the results of these determinations certain relations have been deduced between the osmotic pressure and the depression of the freezing point.

In an earlier paper (Abstr., 1903, ii, 272), a list is given of a number of electrolytically deposited substances which exhibit considerable osmotic activity. The following compounds are also found to possess this property: ferric phosphate, stannous and nickel ferrocyanides, and the cobalticyanides of cobalt, nickel, iron, copper, zinc, cadmium, and manganese. E. G.

Molecular Weights of Metallic Chlorides. LEOPOLD RÜGHEIMER and E. RUDOLFI (*Annalen*, 1905, 339, 311—349).—The use of bismuth chloride as a solvent in determining the molecular weights of metallic chlorides has previously been described in a preliminary account (Abstr., 1903, ii, 725). The method now employed is that given in this vol., ii, 571. In addition to the earlier results, it has been found that molecules of salts in which two metallic atoms are linked together are of very rare occurrence. Only in the case of tin triethyl, which has the molecular formula Sn_2Et_6 , is the double formula beyond doubt.

K. J. P. O.

Molecular Weight of Bismuth Phosphate. LEOPOLD RÜGHEIMER (*Annalen*, 1905, 339, 349—350. Compare preceding abstract).—Since the determination of the molecular weights of salts in solvents possessing a common anion gave good results, attempts were made to ascertain the molecular weight of bismuth phosphate in bismuth chloride, that is, the solvent and the solute having a common cation. The values found were 261.5 and 326.5, whereas BiPO_4 requires 303.5. The phosphate is only sparingly soluble in the chloride.

K. J. P. O.

Explosion Waves. HAROLD B. DIXON (*Ber.*, 1905, 38, 2419—2446).—A lecture delivered before the German Chemical Society. G. Y.

Reaction Velocity and Chemical Equilibrium in Homogeneous Systems and their Bearing on Cases of Enzyme Action. ARIE W. VISSER (*Zeit. physikal. Chem.*, 1905, 52, 257—309. Compare this vol., ii, 511).—Formulae are deduced for the velocities of mono-, di-, and tri-molecular reactions in cases where a point of equilibrium is reached short of complete change. The formula in the case of a uni-molecular reaction is $a = 1/t \cdot \log_e(C_0 - \beta)/(C - \beta)$; C_0 is the initial concentration of the substance undergoing change, C its concentration after time t ; $a = k_1 + k_2$ and $\beta = k_2 C_0 / (k_1 + k_2)$, where k_1 and k_2 are the velocity-coefficients for the opposing reactions. The constant β is shown to be equal to the concentration at the equilibrium point of the substance which is undergoing change. The applicability of the author's formulae is tested with satisfactory results by comparison with Schoorl's data on the formation of dextrose and galactose ureides (see Abstr., 1901, i, 258; 1902, i, 83). The velocity-coefficient in the case of mannose ureide (Schoorl, *loc. cit.*) has constant values whether determined from the dimolecular or the trimolecular formula.

The hydrolysis of sucrose by invertase and that of salicin by emulsin are regarded as reactions which proceed to an equilibrium point short of complete change, and the author accordingly applies the above-mentioned formulae to these two cases. It is found that the velocity-coefficient increases in the first case, but diminishes in the second case, with the time; that is, the "intensity" of the catalyser varies with the concentration of the reacting substances, and the differential equation for the rate of hydrolysis of sucrose by invertase becomes, accordingly, $-dC/dt = I[k_1 C - k_2(C_0 - C)^2]$, where I is the intensity of the enzyme and a function of C . The actual variation of the intensity is obtained by dividing the course of the reaction into small stages, which are taken separately, and over which the velocity-coefficient may be regarded as constant; the value of the velocity-constant for such a short interval is then a measure of the enzyme intensity during that interval. In this empirical way, the author has traced the dependence of the enzyme intensity on the concentration of the reacting substances, and he finds for the hydrolysis of sucrose by invertase $I = k_3/(4C_0^2 + 2C_0 C + C^2)$, and for the hydrolysis of salicin by emulsin $I = k_3/(4C_0^2 - 2C_0 C - C^2)$. When these expressions are combined with the above differential equation it is possible to represent satisfactorily the course of change in each case.

From the reaction-coefficients it is possible to calculate the equilibrium constants, and the values of the latter so obtained agree with those deduced directly from the equilibrium conditions. The position of the equilibrium point is not affected by changing the concentration of the enzyme, but the velocity with which the point of equilibrium is approached is proportional to the concentration of the enzyme. The intensity of invertase falls off with increasing amounts of either sucrose or invert sugar. Over the temperature interval 0—25°, the reaction-coefficient for the hydrolysis of sucrose by invertase

is twice as great at $T+10^{\circ}$ as at T . The displacement of the equilibrium by a rise of temperature from $0-25^{\circ}$ is very small, in harmony with the fact that the heat effect of the reaction is very small.

The author has found that the activity of invertase and emulsin kept in sterilised solution remains quantitatively the same for several weeks.

J. C. P.

Hydrolysis of Esters in Heterogeneous Systems. HEINRICH GOLDSCHMIDT (*Zeit. Elektrochem.*, 1905, 11, 430—433).—Kremann (this vol., ii, 307) has investigated the hydrolysis of ethyl benzoate and of amyl acetate by sodium hydroxide in aqueous solution, and has drawn the conclusion that the reaction velocity observed is the velocity of solution of the ester. The author points out that this is not the case; the velocity of hydrolysis is comparatively small, so that the aqueous solution is always saturated with the ester. He shows in the case of ethyl benzoate that the velocity observed in the heterogeneous system may be calculated from the solubility of the ester and the velocity of hydrolysis obtained in a homogeneous solution. In the case of amyl acetate, the velocity constant changes gradually as hydrolysis progresses, but this is probably due to the amyl salt being a mixture of isomeric substances having different properties.

T. E.

Autocatalytic Decomposition of Silver Oxide. GILBERT N. LEWIS (*Zeit. physikal. Chem.*, 1905, 52, 310—326).—When silver oxide is kept at a steady temperature above 300° , the rate of decomposition is negligibly small at the start, but gradually increases to a maximum, falling off subsequently until the final disappearance of the oxide. When the oxide is previously mixed with metallic silver prepared from another portion of the same oxide, decomposition at the high temperature is at once appreciable, and the rate of decomposition reaches its maximum much sooner than when the oxide alone is taken. It appears, therefore, that the decomposition is catalytically accelerated by the silver which is formed. The rates of decomposition, however, of different samples of silver oxide differ markedly according to their source. Comparison of experiments made at 327° , 332.5° , 352.2° , and 353.3° with different portions of the same sample of oxide shows that the higher the temperature the greater is the maximum velocity of decomposition, and the shorter the period within which complete decomposition takes place. For a given temperature, it may be supposed that the reaction velocity at any moment is proportional to the quantity of oxide and also to the quantity of silver, that is, $dx/dt = Kx(1-x)$; this may be transformed to $dx/dt = Ke^{Kx}/(1+e^{Kx})^2$, and the curve involved in the last equation corresponds very closely with the experimental curves in which velocity of decomposition is plotted against time. The rate of decomposition increases by about 50 per cent. for a rise of 10° .

It is suggested that the reaction which is catalytically accelerated is $2O = O_2$, and it is possibly this also which determines the rate of change in such reactions as the decomposition of potassium chlorate in presence of manganese dioxide and that of hydrogen peroxide in

presence of platinum. It is shown that the initial addition of platinum black to silver oxide has somewhat the same effect as the initial addition of silver; manganese dioxide also is found to accelerate the decomposition of silver oxide.

The thermostat used in these experiments, and recommended by the author, consisted of an enamelled bath filled with a mixture of potassium and sodium nitrates and surrounded by an asbestos shield. The regulator contained mercury, and the supply of gas to the heating burners was regulated by an electrical device.

J. C. P.

Inorganic Chemistry.

Revision of the Atomic Weight of Iodine. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1905, 27, 876—887. Compare Abstr., this vol., ii, 81).—The ratio of silver iodide to silver bromide and silver chloride has been determined by converting a weighed quantity of pure silver iodide into silver bromide by heating it in a quartz crucible in a current of air and bromine vapour and afterwards converting the silver bromide into the chloride by heating it in a stream of pure dry chlorine. From the ratio $\text{AgI}:\text{AgBr}$, obtained from the results of eight experiments made with four different samples of bromine, the atomic weight of iodine was found to be 126.985 ($\text{Ag}=107.93$; $\text{Br}=79.955$). A series of five determinations of the ratio $\text{AgI}:\text{AgCl}$ gave the atomic weight of iodine 126.982, whilst from a second series of five determinations the value 126.984 was obtained ($\text{Cl}=35.473$. Compare Richards and Wells, Abstr., this vol., ii, 451).

In the earlier paper (*loc. cit.*), determinations were made of the ratios of silver to silver iodide and iodine. The ratio of iodine to silver iodide has now been determined by dissolving a weighed quantity of carefully purified iodine in sulphurous acid and adding as nearly as possible the exact amount of pure silver dissolved in nitric acid. The liquid was tested for an excess of iodine or silver by means of the nephelometer, and the deficiency in either was adjusted until the faint opalescence produced both by hydriodic acid and silver nitrate was equal in both nephelometer tubes. It was found that, as already observed by Köthner and Auer (Abstr., this vol., ii, 81), if the silver nitrate is in excess it is liable to be occluded by the precipitated silver iodide, and in order to obviate this, very dilute solutions were employed and no excess of silver. From the ratio $\text{Ag}:\text{I}$, obtained from the results of eight determinations made with several different samples of iodine and three samples of silver, the atomic weight of iodine was found to be 126.987. Five determinations of the ratio $\text{I}:\text{AgI}$ gave the atomic weight 126.983. In order to determine the ratio $\text{Ag}:\text{AgI}$, the filtrate and washings were evaporated to a small

bulk and the silver in the residue estimated by means of the nephelometer. The quantity of silver found was deducted from the original weight of silver and no correction was applied to the silver iodide for the amount dissolved in the washings. The results of four determinations with two samples of silver gave $I = 126.989$.

The average of the six series of experiments gave 126.985 for the atomic weight, and it is therefore probable that the results obtained in the earlier paper (*loc. cit.*) were slightly too low, owing to the occlusion of silver nitrate by the silver iodide.

The agreement of the results from silver bromide with those of the other series indicates that the value 79.955 obtained by Stas for the atomic weight of bromine is very nearly correct.

The results obtained by Köthner and Aeuer (*loc. cit.*) are discussed, and it is suggested that the value 126.936 for iodine ($Cl = 35.45$; $Ag = 107.93$) is probably too low and that this is due to the occlusion of traces of silver nitrate by the iodide and to an increase of weight in the apparatus during the experiment owing to the action of the hot halogens on the glass. A reply is given to the criticisms of Köthner and Aeuer (this vol., ii, 156) on the author's previous paper on this subject. E. G.

Formation of Ozone by Ultra-Violet Light. FRANZ FISCHER and FRITZ BRAEHMER (*Ber.*, 1905, 38, 2633—2639).—Carefully dried and purified oxygen was subjected to the action of ultra-violet light from the mercury arc lamp described by Fischer (this vol., ii, 568). No ozone is formed at temperatures above 270° and the proportion of ozone in the issuing stream of gas is increased by augmenting the amount, or lowering the temperature, of the cooling water employed. Increase of the intensity of the light causes the proportion of ozone obtained to rise to a maximum and then fall somewhat, probably owing to appreciable decomposition of the ozone by a rise in temperature. By doubling the rate of flow of the oxygen, the absolute amount of ozone formed by the lamp is nearly doubled, although the percentage of ozone in the issuing gas is reduced to about 0.8 of its initial value. The fact that the odour of ozone emitted by Heraeus' quartz-mercury lamp diminishes considerably in intensity soon after the lighting of the lamp is due to the rise in temperature. T. H. P.

Amorphous Sulphur. II. Two Liquid States of Aggregation of Sulphur, S_{λ} and S_{μ} , and their Transition Point. ALEXANDER SMITH, WILLIS B. HOLMES, and ELLIOT S. HALL (*J. Amer. Chem. Soc.*, 1905, 27, 797—820. Compare Abstr., 1903, ii, 139, 284; this vol., ii, 382).—Most of the results of the work described in this paper have been published previously.

When melted rhombic sulphur is heated, viscosity first appears at 159.5° . The absorption of heat connected with the transition occurs at 162.5° and upwards, the liquid becoming viscous at the same moment. Distilled sulphur behaves somewhat differently from crystalline sulphur and appears to be much more liable to become superheated; the viscosity is first apparent at 161.5 — 162° and even then asserts itself rather gradually. These phenomena take place in the same way and at the same temperature whether the sulphur

employed is such as by chilling gives insoluble sulphur, or whether it does not do so owing to its having been treated with ammonia.

The coefficients of expansion of sulphur for short intervals of temperature from 154° to 170° have been determined. An experiment is described in which the separation of the two phases, yellow and brown liquid sulphur, may be observed.

E. G.

Measurements of Equilibrium in the Contact Process of preparing Sulphur Trioxide. MAX BODENSTEIN and WILHELM POHL (*Zeit. Elektrochem.*, 1905, 11, 373—384).—The mixture of air or oxygen and sulphur dioxide was passed over platinum sponge contained in quartz glass tubes and heated in an electric tube furnace. Two tubes were employed, in the first of which the greater part of the reaction occurred; the second was jacketed by a thick silver vessel which served to equalise the temperature and contained a thermo-element; in it equilibrium was completely attained at a definitely known temperature. By keeping the temperature of the first tube higher or lower than that of the second, equilibrium could be attained from both directions. The constant $K = \frac{[\text{SO}_2]^2 \cdot [\text{O}_2]}{[\text{SO}_3]^2}$ was determined at 727° for mixtures in which the ratio $2\text{SO}_2 : \text{O}_2$ varied from 0.21 to 3.97; its value was found to be independent of this ratio and also of the quantity of nitrogen present. The following are the most important numerical results obtained:

Temperature.	K.	Q (cals.).
528	1.55×10^{-5}	
579	7.55×10^{-5}	21,300
627	3.16×10^{-4}	22,500
680	1.12×10^{-3}	21,800
727	3.54×10^{-3}	21,500
789	1.26×10^{-2}	21,700
832	2.80×10^{-2}	21,700
897	8.16×10^{-2}	21,100

The values of Q are calculated from those of K; they agree well with Berthelot's thermochemical result, $\text{SO}_2 \text{ gas} + \text{O} = \text{SO}_3 \text{ gas} + 22,600 \text{ cal.}$ at the ordinary temperature.

T. E.

Oxidation of Atmospheric Nitrogen by the Aid of the Electric Arc. FRANZ VON LEPEL (*Ber.*, 1905, 38, 2524—2533).—A continuation of work previously published (*Abstr.*, 1903, ii, 420; 1904, ii, 251, 725). The apparatus used by the author for the oxidation of atmospheric nitrogen by the electric arc is described in detail. The influence of metallic salts distributed on the cathode in small amount on the yield was examined. The influence of the amount of air admitted into the oven and of the shape of the oven were examined and the results quoted in tabular form.

A. McK.

Reactions in Liquid Ammonia. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1905, 27, 820—851. Compare Franklin and Kraus, *Abstr.*, 1900, ii, 382; Franklin and Stafford, 1902, i, 748).—Attention is drawn to the striking resemblance between the physical properties of water and liquid ammonia. Emphasis is laid on the analogy between

the relations of the acid amides, the metallic amides, and the metallic derivatives of the acid amides to ammonia, and the relations of the ordinary oxygen acids, bases, and salts to water, and a system of nomenclature for the former class of derivatives is suggested. It is proposed that ammonia derivatives which bear to ammonia the relation which ordinary salts, bases, and acids bear to water should be termed ammono-salts (for example, potassium acetamide), ammono-bases (metallic amides, imides, and nitrides), and ammono-acids (acid amides, imides, and nitrides). The term "ammonolysis" is suggested for the designation of a class of reactions in which ammonia plays a part analogous with that of water in hydrolysis. The so-called mercuri-ammonium compounds are classified as (1) compounds related to ammonia as ordinary basic compounds are related to water, such as the infusible white precipitate, NH_2HgCl ; (2) salts with ammonia of crystallisation, such as the fusible white precipitate, $\text{HgCl}_2 \cdot 2\text{NH}_3$; and (3) mixed compounds containing residues basic to both ammonia and water, such as the compound $2\text{HgO} \cdot \text{NH}_3$, prepared by the action of ammonia on mercuric oxide.

Experiments are described which were undertaken to ascertain if new metallic amides, imides, or nitrides could be obtained by metathetic reactions between potassamide and salts of other metals in solution in liquid ammonia. *Silver amide*, AgNH_2 , obtained as a white precipitate when a solution of potassamide is added to an excess of silver nitrate solution, is soluble in solutions of ammonium salts, darkens on exposure to light, and when dry forms dark masses which readily explode with great violence. *Mercuric nitride*, Hg_3N_2 , obtained as a chocolate-coloured precipitate on adding a solution of mercuric iodide or bromide to an excess of potassamide solution, is readily soluble in solutions of ammonium salts in liquid ammonia or in aqueous acids and is very explosive.

Ammono-basic mercuric iodide (mercuric iodonitride, dimercuri-ammonium iodide), NHg_2I , prepared by adding potassamide solution to excess of mercuric iodide dissolved in liquid ammonia, forms a reddish-yellow precipitate which is soluble in ammonia solutions of ammonium salts, and by the further action of potassamide is converted into mercuric nitride; when heated in a closed tube, it decomposes without exploding into mercury and mercuric iodide.

Ammono-basic mercuric bromide (mercuric bromonitride, dimercuri-ammonium bromide), NHg_2Br , obtained as a yellow precipitate by treating a solution of mercuric bromide with a solution of potassamide, is soluble in ammonia solutions of ammonium salts or in aqueous acids, and is converted by potassamide into mercuric nitride.

When mercuric chloride is brought into contact with liquid ammonia, the compound $\text{HgCl}_2 \cdot 12\text{NH}_3$ (Franklin and Kraus, *loc. cit.*) is obtained, which is but slightly soluble in liquid ammonia; at the ordinary temperature, it loses ammonia and becomes converted into the fusible white precipitate, $\text{HgCl}_2 \cdot 2\text{NH}_3$. By the action of ammonia on mercuric chloride, a small quantity of ammono-basic mercuric chloride (the infusible white precipitate), NH_2HgCl , is also formed; this compound is also produced by the action of sodamide on an excess of mercuric chloride.

When potassamide is added to a solution of lead nitrate in liquid ammonia, a white basic salt is first precipitated, but on increasing the quantity of potassamide, the precipitate becomes orange-red, and dissolves if an excess of potassamide is added; similar reactions occur between potassamide and lead iodide. *Lead imide*, PbNH , may be prepared by adding lead iodide solution gradually to a solution of potassamide until a considerable quantity of the orange-red precipitate has been produced, and leaving the precipitate in contact with the liquid for 24 hours. The product thus obtained, when dry, forms a reddish-brown, dense, amorphous mass and is very explosive.

Ammono-basic lead iodide, $\text{NPb}_2\text{I}_2\text{NH}_3$, obtained by adding potassamide solution to a solution of lead iodide and shaking the mixture as long as the lead iodide is in excess, forms a white precipitate which, on heating, loses ammonia and gradually darkens in colour and is not explosive.

When a solution of bismuth iodide or bromide in liquid ammonia is added to a solution of potassamide, *bismuth nitride*, BiN , is obtained as a brown precipitate.

On the addition of excess of aluminium iodide to a potassamide solution, a white precipitate of an ammono-basic product is formed. By the action of potassamide solution on the product formed by treating antimony iodide with ammonia, a substance is obtained which probably consists of impure antimony nitride.

E. G.

Properties of Mixtures of Nitric and Sulphuric Acids. IV.
A. V. SAPOSCHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 374—381. Compare Abstr., 1904, ii, 614).—The author has examined mixtures of nitric acid of sp. gr. 1.40 and sulphuric acid by the methods previously described (Abstr., 1904, ii, 251). The vapour pressure of the nitric acid alone is 1.9 mm. of mercury, and it rises to a maximum of 23.43 mm. for a mixture containing 60.16 per cent. of sulphuric acid, falling to 0.66 mm. when the percentage of sulphuric acid present is 89.94. The proportion of nitrogen in the vapour is 19.3 per cent. for nitric acid of sp. gr. 1.40, this corresponding with the composition $2\text{HNO}_3, \text{H}_2\text{O}$; when 5 per cent. of sulphuric acid is present, the amount of nitrogen in the vapour rises to 22.45 per cent., corresponding with the composition HNO_3 , and this number is practically unchanged by subsequent additions of sulphuric acid.

The sp. gr. of the acid mixtures increases regularly with the proportion of sulphuric acid present until the latter reaches 90 per cent.; more sulphuric acid than this conditions a slight fall in the sp. gr. The specific conductivity falls regularly as the percentage of sulphuric acid rises from 0 to 70; beyond this a slight rise occurs, followed by a rapid fall to zero.

The properties of nitric acids of different concentrations were examined with the following results:

Sp. gr. at 15°/4°.	Percentage composition		Vapour pressure of the nitric acid at 25°.	Percentage nitrogen in the vapour.
	HNO ₃ .	H ₂ O.		
1·5100	98	2	46·2 mm.	23·75
1·4970	92·93	7·07	42·6 „	23·5
1·487	88·65	11·35	29·7 „	23·05
1·462	82·10	17·90	16·64 „	22·62
1·453	78·10	21·90	9·40 „	22·52
1·400	65·30	34·70	1·90 „	19·32

T. H. P.

Supposed Volatility of Silicon Dioxide at the Moment of its Liberation by Strong Acids. CARL FRIEDHEIM and ALFRED PINAGEL (*Zeit. anorg. Chem.*, 1905, **45**, 410—411).—The deficiency of silicon dioxide in the analyses of silicates noticed by Kehrman (*Zeit. anorg. Chem.*, **39**, 48) and Flürscheim (*Zeit. anorg. Chem.*, **39**, 106) is attributed to experimental error.

D. H. J.

The Decomposition of Potassium Chlorate by Hydrochloric Acid; a Reaction of the First Order. E. DAVIDSON (*Zeit. angew. Chem.*, 1905, **18**, 1047—1054).—In the absence of oxygen, the reaction between potassium chlorate and hydrochloric acid is unimolecular. The reaction-coefficient is independent of the concentration of the potassium chlorate.

An increase of temperature accelerates the action, as also does the presence of potassium iodide. The rate of decomposition of the chlorate can be measured only when the hydrochloric acid is in considerable excess, and increases when the amount of hydrochloric acid present is increased.

A. McK.

Causticising Potassium Sulphate. IGNAZ HEROLD (*Zeit. Elektrochem.*, 1905, **11**, 417—430).—The reaction between potassium sulphate and calcium hydroxide is studied. The equilibrium constant $k = [\text{OH}]^2/[\text{SO}_4^{''}]$ is easily shown to be the same as the ratio between four times the cube of the solubility of calcium hydroxide and the square of the solubility of calcium sulphate, provided that both salts are present in the solid condition and that they are supposed to be completely dissociated in their saturated solutions. The solubility of calcium hydroxide at high temperatures is determined by heating water with excess of lime in a steel tube, across the middle of which a partition of several layers of very fine platinum gauze is stretched. By inverting the tube, the saturated solution can be filtered under pressure. The following results are obtained expressed in grams of CaO per litre of saturated solution:

Temperature.	Solubility.
120°	0·305
150	0·169
190	0·084

The equilibrium constants calculated from the solubilities do not agree with those found directly, which is probably due to a rapid

diminution of the dissociation of calcium hydroxide at high temperatures. The compositions of the solutions in equilibrium with calcium hydroxide and calcium sulphate are determined at five temperatures from 0° to 190°. At any one temperature, the values of the ratio $[\text{OH}]^2/[\text{SO}_4]$ diminish as the concentrations of the dissolved salts increase, whilst the effect of increase of temperature is first to diminish the ratio and then to increase it, the minimum being found at about 100°. The ratio of the concentrations of the ions cannot be calculated for lack of data.

Below 100°, potassium calcium sulphate is formed when the concentration of the dissolved salts is increased; the third solid phase thus introduced causes the composition of the solution to become constant.

The bearing of the results on the manufacture of potassium hydroxide is then considered. T. E.

Sodium Perborate. Hydrogen Peroxide in Statu Nascendi. GEORGE F. JAUBERT (*Chem. Centr.*, 1905, ii, 99—100; from *Rev. gen. Chim. pure appl.*, [vii], 8, 163—167).—The original paper contains a description of the therapeutic application of hydrogen peroxide. The preparation of pure solutions of hydrogen peroxide appears to be most readily effected by means of sodium perborate (*Abstr.*, 1905, ii, 26).

[With GASTON LION.]—Sodium perborate may be obtained from its solution in water in the form of rather voluminous, lustrous prisms. One litre of water dissolves about 25.5 grams at 15°, 26.9 at 21°, 28.5 at 26°, and 37.8 at 32°. The aqueous solution is distinctly alkaline, and with potassium permanganate behaves like hydrogen peroxide. At temperatures above 40°, the solution decomposes and oxygen is liberated, but the loss is not great if the temperature does not rise above 60°. Small quantities of magnesium sulphate or ammonium sulphate increase the solubility of the salt, and by adding acids still more concentrated solutions of hydrogen peroxide may be obtained. For technical purposes, sulphuric acid is used, and solutions containing 30 or more vols. are produced. E. W. W.

Preparation of Rubidium and Cæsium. L. HACKSPILL (*Compt. rend.*, 1905, 141, 106—107).—Rubidium and cæsium are prepared by heating a mixture of 3 grams of calcium, broken in small pieces, with 12 grams of fused anhydrous rubidium or cæsium chloride respectively in a wide, V-shaped glass tube at the bend of which is fused a vertical tube connected with a Sprengel pump. The reduction commences at 400—500°, and takes place with sufficient development of heat to volatilise the alkali metal, which is collected and sealed off in the vertical tube. This method is more rapid and gives better yields (10 grams) than the reduction of the alkali hydroxide by means of aluminium or magnesium filings. Lithium chloride is reduced by calcium at a slightly higher temperature; so far, there has been obtained only an alloy of calcium and lithium, from which the latter could not be isolated. G. Y.

Decomposition of Ammonium Nitrite in Aqueous Solution and Analogous Changes. WILHELM BILTZ and WILLY GAHL (*Zeit. Elektrochem.*, 1905, 11, 409—413).—Previous investigators have

employed solutions of ammonium nitrite containing other salts; in order to avoid possible complications due to these salts, solutions of pure ammonium nitrite were heated and the rate of evolution of nitrogen measured. The velocity of the reaction is represented about equally well by the equations of the reactions of the first and second order. By means of van't Hoff's method of comparing the velocities at two different concentrations, it is shown that the reaction is really of the second order. The authors take the view that the change takes place between ammonium nitrite and nitrous acid produced by hydrolysis.

The decomposition of ammonium percarbonate is also investigated. It may be represented by the equation of the unimolecular reaction, although van't Hoff's method shows it to be bimolecular. T. E.

Colloidal Salts. I. Silver Salts. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1905, [ii], 72, 39—56. Compare Abstr., 1904, ii, 31).—Colloidal silver chloride, bromide, iodide, thiocyanate, cyanide, hydroxide, carbonate, chromate, sulphide, phosphate, arsenate, ferrocyanide, and ferricyanide may be formed by adding a silver nitrate solution to the solution of the alkali or hydrogen salt, keeping the hydrosol-forming anion in excess, or reversely keeping the silver ion in excess. No hydrosol formation could be observed by the interaction of silver nitrate and hydrocyanic acid. For each case there is a definite maximum limit of concentration, which is greater for the first than for the second method of formation. The silver salt is precipitated in the "molecular" state if the limit of concentration is exceeded or in presence of an excess of the added solution; this precipitation takes place most sharply with the silver haloids. G. Y.

Effect of Silver Nitrate on the Solubility of Silver Nitrite. RICHARD ABEGG and H. PICK (*Ber.*, 1905, 38, 2571—2574).—The numbers obtained by Naumann and Rücker (this vol., ii, 522) for the solubility product $\text{Ag}^+ \times \text{NO}_2^-$ in the presence of silver nitrate are not constant owing to the fact that the authors have assumed that in a saturated solution of the nitrite all the molecules are ionised. It is now shown that at 25° only 55 per cent. of the nitrite is ionised, and if this is taken into consideration the solubility product for the pure nitrite = 2.1×10^{-4} , and it retains the same value in the presence of varying amounts of silver nitrate. At 18°, a value 1.8×10^{-4} has been obtained for the product. J. J. S.

Decomposition of Zinc Carbonate by Solutions of Alkali Chlorides. H. CANTONI and J. PASSAMANIK (*Ann. Chim. anal.*, 1905, 10, 258—262. Compare Abstr., 1904, ii, 334; 1905, ii, 87, 115).—Tables are given showing the action of ammonium, potassium, and sodium chlorides in aqueous solutions on zinc carbonate at different temperatures and periods of action. Experiments with cadmium carbonate are also communicated.

The action of ammonium chloride differs essentially from the other chlorides as it increases very notably with the temperature.

L. DE K.

Co-ordinates of the Melting-point Curve, Change of Volume and Heat of Crystallisation of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in Relation to Pressure. NICOLAI A. PUSCHIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 382—392).—The author has determined the melting point of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at various pressures by the method given by Tammann (*Kristallisieren und Schmelzen*, 1903, 251—263), the results obtained being expressed by the formula: $t = 58.7^\circ + 0.00813p - 0.0000005p^2$. This expression indicates that the maximum of the melting-point curve lies at about 8000 kilos. pressure and 91° ; the value of dT/dp (or Δv) will there pass through zero and subsequently become negative, so that solidification will be accompanied by increase of volume.

The heat of crystallisation of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is found calorimetrically to have the mean value 26.3 Cals. at the ordinary pressure. The author's results satisfy the formula of Clausius, namely, $dT/dp = T\Delta v/R$.
T. H. P.

Spectrographic Investigations of the Urbain-Lacombe Method for the Separation of Samarium, Europium, and Gadolinium. G. EBERHARD (*Zeit. anorg. Chem.*, 1905, 45, 374—384).—A spectrographic test of the efficiency of the Urbain-Lacombe method (*Abstr.*, 1904, ii, 37, 173, 340; this vol., ii, 250) was made with specimens furnished by Urbain himself. The results obtained show that (1) a quantitative separation of europium from samarium is possible by the method, and it forms a good means of preparing pure europium, samarium free from europium, and gadolinium free from samarium. (2) There is no evidence of a fractionation of samarium into simpler constituents. (3) Urbain's value of the atomic weight of samarium (150.34 with $O=16$) is to be regarded as correct since his material was spectroscopically pure. (4) The atomic weight alone cannot serve as a test of the purity of a samarium preparation; Bettendorff found an atomic weight of 150.1, although his preparation was contaminated with a large proportion of gadolinium and with small proportions of neodymium, europium, and yttrium. (5) Gadolinium, even when it yields a white oxide, may still contain small quantities of coloured earths which can be detected spectroscopically.

The conclusions arrived at differ in essential particulars from those obtained by Crookes (this vol., ii, 250, 392). It is suggested that the experimental error in his experiments, due to optical errors of the spectrometer, is greater than Crookes supposes.
D. H. J.

Tensile Strength of Copper-Tin Alloys. E. S. SHEPHERD and G. B. UPTON (*J. Physical Chem.*, 1905, 9, 441—476).—The freezing-point curve of alloys containing more than 50 per cent. copper is given. This shows equilibria fields for the following crystals: α and liquid, β and liquid, γ and liquid. At lower temperatures below the line at which solid alone exists, fields of equilibrium of α , $\alpha + \beta$, β , $\beta + \gamma$, γ , $\alpha + \delta$, δ , $\delta + \text{Cu}_3\text{Sn}$, $\text{Cu}_3\text{Sn} + \epsilon$, are plotted. The only compound existent is Cu_3Sn , the other crystals being solid solutions. The effect of heat treatment of various kinds on the tensile strength and ductility of the alloys has been investigated, and a full account of the method of testing and of the preparation of test pieces is given. Curves of

tensile strength are given. Until 87 per cent. copper is reached there is practically no effect due to heat treatment, as at all temperatures the stable form is the α -crystal. From 87 to 76 per cent. heat treatment has a marked effect; thus alloys annealed at 400° consist of α - and δ -crystals, whilst those annealed at 540° and quenched at a red heat consist of α - and β -crystals and possess a much greater tensile strength. This is very marked at 78 per cent. copper, which when water-quenched at a red heat possesses double the strength of that kept for a week at 400° . In alloys possessing no α -crystals, the tensile strength is very small, and the strongest bronzes are those containing 78 to 81 per cent. copper and consisting of mixtures of α - and β -crystals. When tested as cast, the ductility decreases with decreasing copper content, and heat treatment may increase the ductility very greatly even when it has no effect on the tensile strength; this is especially marked in alloys of 88—90 per cent. copper, for which the ductility may be increased almost four-fold.

L. M. J.

Preparation of Binary Compounds of Metals by the Alumino-thermic Method. CAMILLE MATIGNON and R. TRANNOY (*Compt. rend.*, 1905, 141, 190. Compare Colani, this vol., ii, 525).—The authors have prepared phosphides, arsenides, silicides, and borides by means of reduction with aluminium and are able to confirm Colani's results (*loc. cit.*).

The phosphides of copper, manganese, iron, and nickel are prepared from the phosphates mixed with the corresponding oxide. The arsenides are obtained similarly from the arsenates. Silicides of manganese, chromium, copper, nickel, cobalt, and iron are formed by inducing the reaction in the strongly heated mixture of metallic oxide, silica, and aluminium.

Manganese boride, formed from boric anhydride and manganese oxide mixed in the proportion Mn : B, is obtained as a mass of needles. Boride of iron prepared in the same manner consists of prismatic needles and is extremely difficult to fracture.

In these preparations, in order to obtain the product well separated from the gangue, the initial temperature of the reaction must be about 1000° .

G. Y.

Aluminium-Zinc Alloys. E. S. SHEPHERD (*J. Physical Chem.*, 1905, 9, 504—512).—The specific volume curve for alloys of aluminium and zinc, although it does not diverge greatly from the straight line, consists of two branches which meet at about the composition 50 per cent. aluminium. This indicates the probability that the composition of the phases is approximately pure zinc and a solid solution of zinc in aluminium with a limiting concentration of about 50 per cent. (Care was taken to ensure that the specimens employed had actually reached equilibrium.) Microscopic examination of the alloys confirms the view of the existence of this solution, so that from these results and those of Heycock and Neville on the freezing point the author considers it established that in this series of alloys there are no definite compounds but that two series of solid solutions occur: (1) zinc in aluminium with a limiting concentration of about 50 per cent. zinc,

and (2) aluminium in zinc with a limiting concentration of about 4 per cent. aluminium, these limits being for the temperature 217°. An equilibrium diagram illustrative of these views is given.

L. M. J.

Ultramarine. KARL A. HOFMANN and W. METZENER (*Ber.*, 1905, **38**, 2482—2486).—Ultramarine is not altered by digestion at the laboratory temperature with 98.5 per cent. sulphuric acid, or with fuming sulphuric acid, or with a mixture of nitrosylsulphuric and fuming sulphuric acids. On digestion with 93 per cent. sulphuric acid, a change in the colour of ultramarine is observable in twelve hours, with 89 per cent. acid in three hours, and with 65 per cent. acid in five seconds, the ultramarine being completely decolorised on digestion with the last acid for one hour.

The composition of ultramarine is not altered on digestion at the laboratory temperature with (a) a mixture of glacial acetic acid and acetic anhydride, (b) glacial acetic acid and acetic anhydride saturated with hydrogen chloride or bromide, (c) a solution of bromine in glacial acetic acid and acetic anhydride, or (d) aqueous sodium hydroxide. With acetic acid containing water, decolorisation takes place more quickly than with sulphuric acid containing the same percentage of water. After repeated washing with a solution of hydrogen bromide in acetic acid, the ultramarine residue is found to contain a diminished proportion of sodium and aluminium oxides.

Alkali polysulphides and thiosulphates are decomposed immediately by acetic acid, acetic anhydride, concentrated or fuming sulphuric acid, or a mixture of fuming sulphuric acid and fuming nitric acid, which has no action on ultramarine.

The authors consider ultramarine to be an analogue of Weber's sulphur sesquioxide, S_2O_3 . G. Y.

Changes of Colour caused by the Action of Certain Rays on Glass. SAMUEL AVERY (*J. Amer. Chem. Soc.*, 1905, **27**, 909—910).—It has been observed by Crookes (*Chem. News*, 1905, **91**, 73) that certain glass from South America containing manganese becomes violet on exposure to the sun's rays. The author has obtained samples of glass from New Mexico which were intensely coloured, a bottle partly buried showing the greatest change of colour where most exposed to sunlight. Different samples which had been probably exposed for several years showed a depth of colour approximately proportional to the amount of manganese present. The sand from New Mexico was not radioactive and the change was therefore not due to radium. Similar phenomena have been observed by Fischer (this vol., ii, 320) with ultra-violet rays from a mercury vapour lamp. E. G.

The Action of Slightly Alkaline Waters on Iron. CECIL H. CRIBB and FRANCIS W. F. ARNAUD (*Analyst*, 1905, **30**, 225—237).—The authors find that when the alkalinity of a softened water exceeds a certain limit, the water has no action whatever on bright iron surfaces. With an alkalinity not exceeding a certain amount (dependent on the nature of the alkali present, and, to a less extent, on the temperature), the corrosive action may be equal in intensity to

that which would occur in the absence of any alkali. The hydrogen peroxide theory (Dunstan, Proc., 1903, 19, 150) and the carbon dioxide theory (Moody, Proc., 1903, 19, 157 and 239) are not considered by the authors to explain the corrosive action of these waters on iron. That "pitting" of boilers is not universal where alkaline waters are used is due to the fact that corrosion is less energetic in the dark, and that the boiler plates soon become covered with a more or less protective coating.

L. ARCHBUTT, in an *addendum* (*ibid.*, 241—242) to the above paper, considers that the chief corrosive agent may be carbon dioxide, the action of which ceases when sufficient alkali is present. To prove the contrary, it is necessary to show that distilled water, free from every trace of carbon dioxide, is more corrosive to iron when slightly alkaline than when no alkali has been added. W. P. S.

Properties, Analysis, and Classification of Ternary Steels. LÉON GUILLET (*Compt. rend.*, 1905, 141, 107—108. Compare Abstr., 1903, ii, 297, 483, 650, 730; 1904, ii, 128, 266, 619, 664, 739).—The author's micrographical investigations of special steels have shown that these ternary steels may be grouped in the following classes: (1) perlitic; (2) martensitic, including troostitic; (3) γ -iron; (4) carbide; and (5) graphitic steels.

Important conclusions as to the constitution of the steels, and as to such of their properties as are of interest from an industrial point of view, have been drawn from the microstructure, the inferences being uncertain only in the case of the perlitic group. G. Y.

Transformations of Hydrated Ferric Sulphate. ALBERT RECOURA (*Compt. rend.*, 1905, 141, 108—110. Compare this vol., ii, 527).—When exposed to the air for some days, a concentrated solution of ferric sulphate deposits a spongy, nodular, saffron-yellow mass consisting of the basic sulphate, $6\text{Fe}_2(\text{SO}_4)_3 \cdot \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, impregnated with an acid sulphate of variable constitution which can be removed by extraction with absolute alcohol. Of a specimen of the yellow mass having the composition $\text{Fe}_2(\text{SO}_4)_3 \cdot 11\text{H}_2\text{O}$, 89 per cent. of the iron remained in the form of the basic sulphate after treatment with alcohol. If the yellow mass is allowed to dry in air until it has reached the composition $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, the basic and acid sulphates recombine, and can no longer be separated by alcohol. The solidification of ferric sulphate on evaporation of its solutions takes place therefore in two stages. In consequence of this the yellow mass is not homogeneous, but contains in some parts an excess of the basic, in others of the acid salt. If this is made into a paste with a little water and spread on a plate, at the end of 24 hours the ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, is obtained as a white, homogeneous layer.

The white and yellow hydrated ferric sulphates must differ in constitution. The yellow sulphate dissolves immediately in water, but the white modification does so only slowly. Whilst both sulphates are soluble in absolute alcohol without decomposition, the yellow modification is decomposed to the insoluble basic sulphate

and the soluble acid sulphate, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$, on treatment with alcohol (96 per cent.), or with a little water, or on exposure to moist air, under which conditions the white modification is stable.

The yellow and white hydrated sulphates, as well as the anhydrous sulphate, yield identical solutions when dissolved in water.

G. Y.

Alkaline Cobaltous Solutions. CARL TUBANDT (*Zeit. anorg. Chem.*, 1905, 45, 368—373).—Metallic cobalt is not attacked either when hot or when cold by potassium or sodium hydroxide; if it is exposed, however, as anode to an electric current, it dissolves in the alkaline liquid. The most favourable conditions for this solution are low current density (0.2 ampere per sq. dm.), high temperature, and great concentration of the alkali hydroxide solution. By inserting a copper voltameter into the circuit and comparing the separated copper with the dissolved cobalt, it is shown that the cobalt dissolves as cobaltous salt.

The cobaltous solution is blue, and in absence of air is stable for months. When electrolysed between insoluble electrodes, it precipitates part of the cobalt at the cathode as spongy metal, part at the anode as oxide; the chief part is oxidised by the oxygen given off at the anode, and the oxidation product remains suspended in the form of brown flocks in the electrolyte. An experiment in which the blue liquid is placed in a U-tube, covered with a layer of alkali hydroxide, and electrolysed with a current of 0.1 ampere shows that the cobaltous oxide migrates towards the cathode.

The cobaltous oxide is thrown down completely by shaking with barium sulphate, but is not appreciably affected by the addition of electrolytes. It does not dialyse, and is believed by the author to be present in the colloidal form.

As regards dialysis, electrolysis, and behaviour with barium sulphate, the blue alkaline cobaltous solutions containing glycerol and the green cobaltic solutions formed from them by oxidation with air or hydrogen peroxide behave similarly to these alkaline cobaltous solutions, and they also are believed to be of a colloidal character. D. H. J.

Passivity of Nickel. MARIO G. LEVI (*Gazzetta*, 1905, 35, i, 391—405. Compare Hittorf, *Abstr.*, 1900, ii, 705; Le Blanc and Schick, *Abstr.*, 1904, ii, 229; Le Blanc and Bindschedler, *Abstr.*, 1902, ii, 442; Just, *Abstr.*, 1903, ii, 629).—The author has measured the loss in weight of a nickel anode and the voltage at the electrodes in 1.5 per cent. solutions of a number of salts at the ordinary temperature, and with an anodic current density of 0.5 ampere per sq. dm. The results show that ordinary nickel dissolves quantitatively according to Faraday's law in solutions containing halogen salts, potassium cyanide, or sulphuric acid, whilst in sodium chlorate or nitrate, barium or cupric nitrate, sodium, ammonium, magnesium, or nickel sulphate, sodium carbonate, potassium hydroxide, or ammonium oxalate, it remains practically undissolved. In sodium acetate solution, about 50 per cent. of the theoretical quantity of nickel dissolves; the greater or less activity of the nickel in this solution depends on the treatment

to which the electrode has been subjected before electrolysis and on the physical condition of its surface.

Experiments with nickel electrodes which have undergone various preliminary treatments show that this metal tends to become passive when left for some time to itself. This phenomenon has been previously noticed in the case of chromium.

For the salt solutions examined, the activity or inactivity of the nickel depends only on the nature of the anion, and not on that of the cation, with the sole exception of the hydrogen ion.

As with other metals, rise of temperature favours the passage of nickel from the passive to the active state, and only in potassium hydroxide solution is nickel completely passive at 80°. In solutions of sodium acetate or ammonium sulphate, it retains at 80° the partial activity it shows at the ordinary temperature.

By increasing the current density, nickel is rendered more passive, but change of concentration of the electrolyte is without influence in this respect.

If the passivity of a metal depends on the formation of an insoluble coating, it should be removed by the addition of the solution of another salt, the anion of which forms with the metal a readily soluble salt. The behaviour of nickel in such mixtures of electrolytes indicates that the passivity of the metal in sodium carbonate or potassium hydroxide solution may be due to the formation of a protective layer. This could, however, not be observed in the other solutions examined, so that here the passivity appears to be due to the smallness of the reaction velocity. A small addition of sodium chloride to a solution causing passivity brings the velocity of ion-formation up to the value required for the quantitative solution of the metal. Sulphuric acid also acts in this way, but to a less extent than sodium chloride. Addition of sugar or acetone is without influence, but carbamide destroys the passivity, although it is uncertain whether its action is a direct one or whether it is due to its decomposition products. T. H. P.

A Chromium Sulphate in which the Acid is in Two States of Combination. ALBERT COLSON (*Compt. rend.*, 1905, 141, 119—122. Compare this vol., ii, 94, 460).—The green chromium sulphate solution, formed by shaking chromium hydroxide with a limited quantity of cold dilute sulphuric acid, has the composition $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$; when evaporated in a vacuum it yields an amorphous substance which dissolves in alcohol (90 per cent.) to a solution containing chromium and sulphuric acid in unchanged proportion. Of the five SO_4 groups present, only three are immediately precipitated by barium chloride; the addition of 1 mol. or 3 mols. of barium chloride to 1 mol. of the sulphate causes immediate precipitation of barium sulphate, with a heat development of 5 and 15.2 Cal. respectively; the addition of 4 mols. of barium chloride to 1 mol. of the sulphate $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ causes a heat development of only 15.5 Cal.; the solution clears only slowly and contains the elements of barium sulphate at the end of fifteen days or after some minutes' boiling.

The difference in the states of combination of the SO_4 groups can be only slight, as the heat of formation of the sulphate $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$

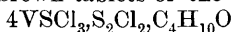
is 12—16 Cal. for each mol. of sulphuric acid entering into the reaction, as the salt is completely hydrolysed by potassium hydroxide, and as the resistance to precipitation with barium chloride is not constant, diminishing with rise of temperature, increase of concentration, or addition of an excess of barium chloride.

The constitution $\text{SO}_4\left(\text{Cr}\begin{smallmatrix}\text{SO}_4\\ \text{O}\end{smallmatrix}\text{Cr}\cdot\text{SO}_4\text{H}\right)_2$ is suggested for the penta-sulphate; in agreement with this, measurements of the depression of the freezing points of the solutions show that on total precipitation with barium chloride, 1 mol. of the sulphate $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ yields 4 mols. of chloride. G. Y.

The Preparation of Metallic Vanadium and some Vanadium Compounds. IWAN KOPPEL and A. KAUFMANN (*Zeit. anorg. Chem.*, 1905, 45, 352—358).—Vanadium prepared by the action of aluminium (Goldschmidt's process) is not pure (from 78.2—81.1 per cent. of vanadium), but serves admirably for the preparation of a mixture of vanadium tetrachloride and oxytrichloride by treatment with chlorine. The two chlorides are easily separated by fractional distillation.

Vanadium oxytrichloride, VOCl_3 , is soluble in ether or glacial acetic acid, but insoluble in chloroform. It may be prepared in solution by shaking vanadium pentoxide with glacial acetic acid into which hydrogen chloride has been passed. Ether or alcohol may take the place of the acetic acid, but the temperature must be kept down in this case to prevent the formation of VOCl_2 by reduction. On adding pyridine hydrochloride to the alcoholic solution of vanadium oxytrichloride, brown, shimmering, hygroscopic needles of the compound $\text{VOCl}_3\cdot\text{C}_5\text{NH}_5\text{Cl}\cdot\text{C}_2\text{H}_6\text{O}$ are obtained.

Vanadium Thiotrichloride.—When chlorine is passed first in the cold, then at a higher temperature, over vanadium sesquisulphide, a reddish-brown liquid of the composition $4\text{VSCl}_3\cdot\text{S}_2\text{Cl}_2$ passes over. The liquid solidifies in a freezing-mixture to a mass of shimmering crystals which decompose in the air with separation of sulphur chloride. From a solution in ether, large, brown tablets of the composition



gradually separate. All attempts to obtain the simple thiotrichloride, VSCl_3 , have so far failed. D. H. J.

Compounds of Quadrivalent Vanadium. III. IWAN KOPPEL, RESZÖ GOLDMANN, and A. KAUFMANN (*Zeit. anorg. Chem.*, 1905, 45, 345—351).—From vanadyl chloride, two series of double salts are obtained with pyridine or quinoline hydrochloride, namely:

(a) Green salts: $\text{VOCl}_2\cdot 4(\text{R}, \text{HCl}), x\text{H}_2\text{O}$.

(b) Blue salts: $\text{VOCl}_2\cdot 2(\text{R}, \text{HCl}), x\text{H}_2\text{O}$.

The green compounds are formed in presence of excess of pyridine or quinoline hydrochloride with solvents which show very little ionisation (absolute alcohol, glacial acetic acid, or mixtures of alcohol and ether). As soon as the power of dissociation of the alcohol is slightly increased by addition of water, the blue compounds are formed. The differences in the dissociation of vanadyl chloride in different solvents are marked by differences in the colour of the solutions.

Solutions of vanadyl chloride (or of vanadium tetrachloride) in absolute alcohol or glacial acetic acid are brown; by the addition of a little water they become green, and finally blue like the aqueous solutions.

Vanadyl chloride-tetrapyridine hydrochloride, $\text{VOCl}_2, 4\text{C}_5\text{NH}_5\text{Cl}, 2\text{H}_2\text{O}$, forms green, hygroscopic needles. It cannot be recrystallised unchanged, as small quantities of water or alcohol change it into the blue compound.

Vanadyl chloride-dipyridine hydrochloride, $\text{VOCl}_2, 2\text{C}_5\text{NH}_5\text{Cl}, 3\text{H}_2\text{O}$.—The blue vanadyl chloride solution necessary for preparing this compound is obtained by evaporating a solution of vanadium pentoxide in hydrochloric acid and dissolving the residue in absolute alcohol or by heating vanadium pentoxide with alcoholic hydrogen chloride and some water in presence of sulphur dioxide or hydroxylamine hydrochloride as reducing agent. On adding pyridine hydrochloride to the blue alcoholic solution and evaporating over sulphuric acid or precipitating with ether, blue hygroscopic needles are obtained. It is more stable than the green compound.

Vanadyl chloride-tetraquinoline hydrochloride,
 $\text{VOCl}_2, 4\text{C}_9\text{NH}_8\text{Cl}, 2\frac{1}{2}\text{H}_2\text{O}$,
 forms green, silky needles, and is more stable and less hygroscopic than the corresponding pyridine salt. From its alcoholic solution, the blue chloride (*vanadyl chloride-diquinoline hydrochloride*),

$\text{VOCl}_2, 2\text{C}_9\text{NH}_8\text{Cl}, 4\frac{1}{2}\text{H}_2\text{O}$,
 crystallises.

Vanadyl ammonium carbonate, $7\text{VO}_2, 5\text{CO}_2, 3(\text{NH}_4)_2\text{O}, 16\text{H}_2\text{O}$, is obtained by dissolving ammonium metavanadate in the minimum quantity of sulphuric acid and reducing with sulphur dioxide, neutralising with ammonia, and, after evaporating to a small bulk, dropping slowly into a cold saturated solution of ammonium carbonate until the precipitate formed redissolves only slowly. The liquid is then filtered and concentrated over sulphuric acid. It forms violet crystals somewhat sparingly soluble in water, soluble in alkalis to a brown solution, and in acids to a blue solution; even in closed vessels it decomposes slowly with evolution of ammonia. D. H. J.

Hydrolysis of Stannic Chloride and Stannic Bromide. PAUL PFEIFFER (*Ber.*, 1905, 38, 2466—2470. Compare Werner and Pfeiffer, *Abstr.*, 1898, i, 464).—If a 50 per cent. solution of stannic chloride, freshly prepared by dissolving the salt in water externally cooled by ice, is shaken with ether and the ethereal solution dried and evaporated, 29 per cent. of the salt is obtained as the *hydroxytrichloride*, $\text{SnCl}_3 \cdot \text{OH}, \text{H}_2\text{O}, \text{Et}_2\text{O}$. Only traces of this are obtained from stannic chloride solutions which have been prepared some hours before extraction. On solution in ether and precipitation with light petroleum, it forms colourless, deliquescent crystals melting and decomposing at 160° , and decomposing when dissolved in water. The *hydroxytribromide*, $\text{SnBr}_3 \cdot \text{OH}, \text{H}_2\text{O}, \text{Et}_2\text{O}$, obtained in the same manner from stannic bromide, forms compact, transparent, colourless, deliquescent crystals melting and decomposing at about 110° . These hydroxyhaloids are the first

intermediate products in the hydrolysis of stannic haloids to stannic acid.

The action of absolute alcohol on stannic bromide leads to the formation of the ethoxytribromide, $\text{SnBr}_3 \cdot \text{OEt}, \text{EtOH}$, previously described ; it crystallises in glistening, colourless leaflets and melts and decomposes at about 160° . G. Y.

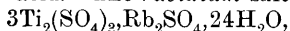
Titanium. II. ARTHUR STÄHLER and, in part, HEINZ WIRTHWEIN (*Ber.*, 1905, **38**, 2619—2629. Compare this vol., ii, 40).—For the preparation of pure titanium compounds, the author makes use of rutile (TiO_2), titanium iron ore (FeTiO_3), and yttritanite, the finely-powdered mineral being mixed with charcoal and fused in an electric furnace to form the carbide, which is then treated with chlorine at an incipient red heat. The crude titanium chloride is then freed from chlorine by distillation and from vanadium by shaking with a little sodium amalgam for forty-eight hours, after which it becomes quite colourless. After further distillation in a vacuum, it boils at 136° (uncorr.). When rutile is heated with sulphur monochloride, the iron and vanadium are first given off as chlorides, almost pure titanium oxide remaining. The latter then becomes converted slowly into titanium chloride, which cannot, however, be separated from the excess of sulphur monochloride owing to the slight difference between the boiling points of the two compounds.

It is generally stated that solutions of quadrivalent titanium give a yellow colour with ether in presence of alcohol. The author finds, however, that this is only the case when the ether contains hydrogen peroxide ; the presence of alcohol is unnecessary.

Dilute aqueous solutions of titanium sesquichloride have a pale wine-red colour, which is changed to dark violet or blue by the addition of an acid ; this behaviour can be made use of to control the purity of the titanium sesquichloride. If a quadrivalent titanium compound is present, it is decomposed on boiling into colloidal titanous acid and free acid, which then produces the above blue coloration. The green titanium sesquichloride, $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, cannot be obtained by Glatzel's method (*Abstr.*, 1877, i, 688), which yields a hydrate of titanium dichloride. If, however, a concentrated aqueous solution of the violet hydrate of the sesquichloride is covered with a layer of absolute ether and then saturated with hydrogen chloride and kept cool meanwhile, the green, unstable hydrate separates out in crystals ; when the hydrogen chloride is washed out with ether, the violet compound is again formed. Green vanadium sesquichloride does not change in colour when treated with ethereal hydrogen chloride.

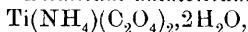
Solution of titanium in sulphuric acid and evaporation of the liquid does not yield the violet sulphate, $\text{Ti}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, as was stated by Glatzel (*loc. cit.*), but titanous sulphate (compare Wohler and St. Claire Deville, *Annalen*, 1857, **103**, 230). By repeatedly evaporating a concentrated solution of titanium sesquichloride with dilute sulphuric acid in a vacuum, a crystalline precipitate is obtained which, after shaking with acetic acid and washing with ether, is found to be *titanium sesquisulphate sulphuric acid*, $3\text{Ti}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 25\text{H}_2\text{O}$. This acid may be quantitatively separated by heating titanium tetrachloride gently with sulphuric acid until fuming ceases, dissolving the resulting syrupy

titanium sulphate in 50 per cent. sulphuric acid, and electrolytically reducing the solution for five to six hours. The acid is obtained as a violet, finely crystalline, silky powder, which slowly dissolves in water giving a violet solution. When heated, water is first evolved, then sulphuric acid, the residue becoming green in colour; at a low red heat, sulphur dioxide is evolved and titanium dioxide remains. The ammonium salt, $3\text{Ti}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$, forms stable, pale blue, microscopic crystals and is insoluble in water or sulphuric acid, but soluble in hydrochloric acid. The rubidium salt,



was also isolated. *Titanium sesquisulphate*, $\text{Ti}_2(\text{SO}_4)_3$, deposited after protracted evaporation of the violet solution of titanium sesquisulphate sulphuric acid with dilute sulphuric acid in absence of air, is a green, crystalline powder insoluble in water, alcohol, ether, or concentrated sulphuric acid, but soluble in dilute sulphuric or hydrochloric acid giving a violet solution.

Tervalent titanium forms a series of oxalates which differ from those of chromium and vanadium in being sparingly soluble in water. The *sesquioxalate*, $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, forms yellow, oblique-ended prisms and is soluble in water. *Titanium ammonium oxalate*,



titanium potassium oxalate, $\text{TiK}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, and *titanium rubidium oxalate*, $\text{TiRb}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, were also prepared.

On repeating the experiments of Rosenheim and Schütte (Abstr., 1901, ii, 244) on the action of dry ammonia on titanium chloride suspended in absolute ether, the author obtained a yellow powder which has approximately the composition $\text{TiCl}_4 \cdot 8\text{NH}_3$, but gives up ammonia very readily. The action of ammonia on gaseous titanium tetrachloride yields the compound $\text{TiCl}_4 \cdot 6\text{NH}_3$ (compare Rosenheim and Schütte, *loc. cit.*), which remains unaltered over freshly ignited calcium chloride in absence of air, but changes to titanous acid, ammonium chloride, and ammonia over ordinary calcium chloride or in presence of air. When titanium tetrachloride is shaken for twelve hours with liquid ammonia, the compound $\text{TiCl}_4 \cdot 8\text{NH}_3$ is obtained as a pale yellow powder. When either $\text{TiCl}_4 \cdot 6\text{NH}_3$ or $\text{TiCl}_4 \cdot 8\text{NH}_3$ is extracted with liquid ammonia, it gives up ammonium chloride and yields dark yellow titanamide, $\text{Ti}(\text{NH}_2)_4$. T. H. P.

The Reduction of Zirconium Oxide and the Spontaneous Formation of Zirconium Nitride. EDGAR WEDEKIND (*Zeit. anorg. Chem.*, 1905, 45, 385—395).—It was not found possible to obtain zirconium by the action of aluminium on the oxide; the reaction is difficult and incomplete. When the oxide is heated with magnesium in a loosely covered crucible, the product is chiefly zirconium nitride, Zr_2N_3 , together with a substance which forms a blue colloidal solution with water. After purification, the zirconium nitride forms a brownish-green, crystalline powder which, even on slight heating in the air, oxidises with incandescence, but is very stable towards both acids (except hydrofluoric acid) and alkalis. It is easily attacked at a low red heat by chlorine, and zirconium chloride is readily prepared in this way, although the yield is not good. It is acted on still more readily by

bromine, and zirconium tetrabromide may very advantageously be prepared by this method. In the form of a compressed powder, the nitride does not conduct an electric current. D. H. J.

Zirconium Halogen Compounds. ARTHUR STÄHLER and BRUNO DENK (*Ber.*, 1905, **38**, 2611—2618. Compare *Abstr.*, 1904, ii, 345; Matthews, *Abstr.*, 1899, 295, 296).—When dry ammonia gas is passed over anhydrous zirconium chloride at the ordinary temperature, the compound $\text{ZrCl}_4 \cdot 8\text{NH}_3$ is obtained as a loose, white powder, extremely hygroscopic and readily decomposed by water. At higher temperatures (232°), a compound $\text{ZrCl}_4 \cdot 3\text{NH}_3$ appears to be formed. The bromide yields a compound $\text{ZrBr}_4 \cdot 10\text{NH}_3$. The iodide yields with gaseous ammonia the following compounds: at 22° , $\text{ZrI}_4 \cdot 8\text{NH}_3$; at 100° , $\text{ZrI}_4 \cdot 7\text{NH}_3$, and at 150° , $\text{ZrI}_4 \cdot 6\text{NH}_3$. With liquid ammonia, the compound with 8NH_3 is obtained, but when this is washed with liquid ammonia, a considerable amount of ammonium iodide is removed and the percentage of zirconium in the residue increases; it would thus appear that the additive compound is probably a mixture of zirconamide and ammonium iodide, $\text{ZrI}_4 \cdot 8\text{NH}_3 = \text{Zr}(\text{NH}_2)_4 + 4\text{NH}_4\text{I}$ (compare Joannis, *Abstr.*, 1903, ii, 140; Blix and Wirbelauer, *ibid.*, 1904, ii, 120). The iodide also forms an additive compound with ethylamine, $\text{ZrI}_4 \cdot 6\text{NH}_2\text{Et}(\text{?})$, and with ether a compound $\text{ZrI}_4 \cdot 4\text{Et}_2\text{O}$. J. J. S.

Reduction of Thorium Oxide by Amorphous Boron and Preparation of Two Thorium Borides. BINET DU JASSONNEIX (*Compt. rend.*, 1905, **141**, 191—193).—If a mixture of thorium oxide and boron is heated for three minutes in a carbon boat in an electric furnace, with a current of 500 amperes and an *E.M.F.* of 100 volts, the mixture becomes metallic in appearance; fusion takes place only after some minutes with a current of 700 amperes. The bronze-yellow to red product is hard, contains masses of needles, and is only slightly carbonised in the parts next to the boat. With dilute hydrochloric acid, it evolves a mixture of hydrogen, which burns with a green flame, and small quantities of hydrocarbons, leaving a residue consisting of thorium tetraboride or a mixture of this with the hexaboride. Even if the amount of boron in the mixture is exactly sufficient for the reduction, the product contains about 10 per cent. of boron, and on solution in nitric acid it leaves a large residue of the unreduced oxide. If the proportion of boron is increased, the fusion becomes more difficult, but owing to volatilisation the amount of boron in the product does not exceed about 17 per cent.

Thorium tetraboride, ThB_4 , obtained from the product containing not more than 10—12 per cent. of boron, is a yellow, metallic powder, consisting of fragments of prismatic crystals and having a sp. gr. 7.5 at 15° . It is dissolved by cold concentrated hydrochloric acid, by cold nitric acid with formation of boric acid, or by hot sulphuric acid. Below a red heat, it is attacked by hydrogen chloride, by chlorine, or by sulphur with formation of boron and thorium sulphides, and it burns when slightly heated in contact with fluorine.

The bronze-yellow to red product, containing over 12 per cent. of boron, contains a mixture of the borides from which the tetraboride is removed by extraction with concentrated hydrochloric acid. *Thorium*

hexaboride, ThB_6 , is an amorphous, reddish-violet, metallic substance which has a sp. gr. 6.4 at 15° , is not dissolved by concentrated hydrochloric, hydrofluoric, or sulphuric acids, or by aqueous alkali hydroxides, but dissolves easily in hot nitric acid and burns when slightly heated in fluorine. It is attacked by chlorine and oxygen below a red heat, by hydrogen chloride at a red heat, and forms boron and thorium sulphides when heated in sulphur vapour. G. Y.

Occurrence of Palladium and Platinum in Brazil. EUGEN HUSSAK (*Chem. Centr.*, 1905, ii, 107; from *Oesterr. Zeit. Berg.-Hütt.*, 53, 278—279).—The natural occurrence of pure palladium has not been definitely proved. It is generally found as palladium-gold in Seifen and in the Jacutinga of the Itabirite, where the material is rich in gold and occurs without pyrites in the schistose quartz hæmatite layers. The composition of the palladium-gold alloy is very variable, the richest being found in Itabiro do Malto dentro. Pure platinum is often associated with the alloy. The occurrence of palladium-gold at Candonga in a contact limestone renders it probable that the Jacutinga has been formed from limestone by metamorphosis.

For the last 100 years, the most important sources of platinum in Brazil have been the river sands on the eastern slope of the Serra da Espinhaco (Corrego das Lagens, Fazenda Condado) and the diamond sands of the Rio Abaete in the State of Minas. Platinum is very seldom found with palladium-gold in the Jacutinga (Gongo Socco), but it more frequently occurs in the gold-quartz ores of the crystalline schists (Pernambuco). At Corrego das Lagens, platinum occurs in clusters of thin-sided, fibrous, and scaly masses which resemble deposits from solutions. Since the specific gravity is 20.2—20.48, this deposit probably contains iridium. The platinum at Condado may be derived in a similar manner from pyrites containing platinum or from sperrylite; its specific gravity is 15—16, and it probably, therefore, contains palladium. In the diamond sands of the Rio Abaete, the magnetic platinum must be derived from a neighbouring mineral which contains olivine. E. W. W.

Mineralogical Chemistry.

Gravimetric and Spectroscopic Analysis of Zinc Blendes from Sardinia. CARLO RIMATORI (*Atti R. Accad. Lincei*, 1905, [v], 14, i, 688—696).—Results are given of analyses of fifteen samples of zinc blende found in Sardinia. Cadmium is found in all of them, whilst copper is often present. Eight of them contain more than 10 per cent. of iron, and hence consist of the variety marmatite; one of these contains 5.81 per cent. of manganese, which is a larger proportion than has been hitherto found in zinc blende. Two of them contain

small quantities of bismuth, which has previously been met with only in the blends of Joachimsthal. Two of the samples contain indium and gallium at the same time, but more frequently indium only is found.

T. H. P.

Copper-pitch-ore from Amzalar, Roumania. TH. NICOLAU (*Ann. Sci. Univ. Jassy*, 1905, 3, 103—105).—The mineral described occurs with chalcoppyrite, azurite, malachite, chrysocolla, and veins of quartz in a dyke of quartz-porphry traversing phyllite at Amzalar near Balancea in Dobruja. It is dark brown and has the appearance of pitch. Under the microscope, thin splinters are brown and transparent; the material is optically isotropic and apparently homogeneous, there being nothing suggestive of a mixture. The sp. gr. is 3·124, and does not vary in different fragments. After deducting 11·7 per cent. of intimately intermixed chalcoppyrite, the composition is given as follows:

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	Cu.	H ₂ O.	Total.
16·37	0·93	47·64	7·39	0·82	12·46	14·39	100·00

This composition cannot be explained as a mixture of chrysocolla and limonite. Copper-pitch-ore, therefore, appears to be a homogeneous mineral (a result also recently arrived at by Lindgren and Hillebrand, this vol., ii, 97).

L. J. S.

Titanite from Urotva, Transylvania. TH. NICOLAU (*Ann. Sci. Univ. Jassy*, 1905, 3, 169—170).—The following analyses are of dark brown crystals of titanite from the syenite of Urotva (Jolotca), in the eastern part of Transylvania. Calcium is in part replaced by manganese, and iron is absent. The crystals are of two habits, the larger ones (7·5 mm. across) being envelope-shaped and the smaller coffin-shaped.

TiO ₂ .	SiO ₂ .	CaO.	MnO.	Al ₂ O ₃ .	Na ₂ O.	Total.
42·24	31·10	24·30	2·09	0·64	0·06	100·43
42·65	31·03	24·19	2·34	0·55	trace	100·76

L. J. S.

Physiological Chemistry.

Blood Changes following Anti-typhoid Inoculation.. W. B. LEISHMAN, W. S. HARRISON, A. B. SMALLMAN, and F. M. G. TULLOCH (*J. Hygiene*, 1905, 5, 380—427).—The origin and early development of the protective substances and the immediate effect of inoculation and re-inoculation are given with full details. No “negative phase” could be detected. The methods used did not reveal the presence of a typhoid opsonin. Metschnikoff’s term *stimulin* is provisionally

adopted, but the identity of stimulins is not regarded as established; they are thermostable and not to be confused with opsonins. The amount of agglutinins developed affords a good general indication of the development of other protective substances. W. D. H.

Blood-ferments. ADOLF JOLLES and MORITZ OPPENHEIM (*Chem. Centr.*, 1905, i, 1659; from *Virchow's Arch.*, 1905, 180, 185—225. Compare this vol., ii, 265).—Experiments have been conducted in order to determine the influence of various factors on the decomposition of hydrogen peroxide by blood. It is stated that the relative amounts of the catalase present in specimens of blood can be determined by estimating the amount of peroxide decomposed in a given time at a given concentration. The simplest method of estimation is to determine by the thiosulphate or permanganate method the amount of peroxide left undecomposed.

Normal human blood usually decomposes 23 grams of peroxide per 1 c.c. of blood, and the decomposition is retarded both by increase and decrease of temperature and also by the usual enzyme poisons. The amount decomposed appears to be independent of the condition of the hæmoglobin, and the formation of oxyhæmoglobin is independent of the enzyme. The blood of amphibious animals often shows a very low decomposing value, and the blood of fishes gives the lowest of all. J. J. S.

Origin of Lactose. Removal of the Mammary Glands during Lactation. CH. PORCHER (*Compt. rend.*, 1905, 141, 73—75. Compare Abstr., 1904, ii, 424).—Soon after the operation, especially about the fourth and fifth hours, the urine contained much glucose (30—45 grams per litre). After 48 hours, however (sometimes after 12—15 hours), the urine lost its reducing power.

Under normal conditions, the blood transports glucose to the mammary glands, where, in the regular course of lactation, it is converted into disaccharide and is excreted in the milk. The removal of the glands results in an accumulation of glucose in the blood, from which it passes to the urine. The rapid cessation of the transportation of glucose to the urine is attributed to a diminution of the activity of the liver.

The glucose found in the urine is not accompanied by galactose.

N. H. J. M.

Physiological Significance of the Urate Cells in Melliferous Insects. L. SEMICHON (*Compt. rend.*, 1905, 140, 1715—1717).—The urate cells appear early in *Anthophora personata*, *Osmia cornuta*, *Megachile argentata*, *Dasypoda plumipes*, and *Halictus quadricinctus*, as in the case of carnivorous *Hymenoptera*. They seem to be inactive during the whole period of relaxed life. Their formation and increase occur chiefly during the active larval life. N. H. J. M.

Affinity of Colouring Matters for Conjunctive Tissue. CURTIS and PAUL LEMOULT (*Compt. rend.*, 1905, 140, 1606—1608).—In order to develop the selective attraction of conjunctive tissue for certain dyes in preparations stained with picric acid, it is necessary to use dyes

having at least three sulpho-groups symmetrically distributed in the molecule. Satisfactory results are obtained with acid magenta, red-violets 4RS and 5RS, and with diamine-blue 2B and naphthol-black B.
N. H. J. M.

Oxyhæmoglobin of Guinea-pigs. Action of Fluorides. M. PIETTRE and A. VILA (*Compt. rend.*, 1905, 140, 1707—1708. Compare this vol., i, 622).—Oxyhæmoglobin is only spectroscopically sensitive to fluorides in solution. Crystals produced in media containing fluorine do not possess the spectrum characteristic of fluorine.

The sensitiveness of the reaction is so great that it is obtained, in dilute acetic acid solution, with very sparingly soluble fluorides. The reaction was observed in water which had been employed for levigating powdered fluorine minerals, such as cryolite and topaz.

N. H. J. M.

Toxicology of Mercury Diphenyl. ÉMILE LOUISE and F. MOUTIER (*Compt. rend.*, 1905, 140, 1703—1704).—Experiments with dogs showed that mercury diphenyl is less toxic than organo-metallic compounds with fatty groups. The mercury becomes rapidly distributed when injected hypodermically, and continues to be eliminated long after injections have ceased. The toxicity of the mercury is partly masked, whilst its therapeutic properties are maintained.

N. H. J. M.

Pilocarpine and other Reagents in Relation to Precipitin Immunity. ORLANDO INCHLEY (*J. Hygiene*, 1905, 5, 285—303).—The elaboration of specific anti-substances is not appreciably affected by the drugs examined (pilocarpine, sodium cinnamate, nuclein, blood sera, &c.). If a temporary increase is the result, this can be explained in other ways. For instance, in the case of pilocarpine, the concentration of the blood due to general glandular activity will account for the apparent increase in the precipitin reaction.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Lactose Fermenting Bacteria in Fæces. A. MACCONKEY (*J. Hygiene*, 1905, 5, 333—379).—A large number of lactose-fermenting bacilli were found in the fæces both of men and animals. Some of these decompose dulcitol, some do not. Some decompose sucrose, others do not. As the *Bacillus coli communis* is more closely associated with fæces than the other groups, further research on the same lines will probably help to place the value of this organism as an index of pollution on a sound basis. W. D. H.

Nitrogen Bacteria. F. LÖHNIS (*Centr. Bakt. Par.*, 1905, ii, 14, 582—604 and 713—723).—The various nitrogen-assimilating bacteria (*Bacterium pneumoniæ*, *B. lactis viscosum*, *B. radiobacter*,

B. radicola, *B. prodigiosum*, and *B. turcosum*) also assimilate nitrates, but in different degrees. *B. agreste* does not fix nitrogen, but assimilates nitrates vigorously, whilst *B. fluorescens* causes nitrates to disappear, chiefly by denitrification. It is probable that nitrogen in the form of ammonium salts and asparagine, &c., is more readily assimilated than nitrates.

It was found that the soil sample utilised for the above experiments rapidly converted carbamide into ammonium carbonate, owing probably to the presence of *Urobacillus Pasteurii*. Attempts to isolate this microbe were, however, unsuccessful.

N. H. J. M.

Life Conditions of Nitrogen-collecting Bacteria. HUGO FISCHER (*J. Landw.*, 1905, 53, 289—297. Compare this vol., ii, 189).—The conclusion is drawn that the bacterial flora depends chiefly on the nature of the soil, and that the flora can only be influenced by alterations in the character of the soil.

N. H. J. M.

Autofermentation of Beer Yeast. JEAN EFFRONT (*Bull. Soc. Chim.*, 1905, [iii], 33, 847—850).—Yeast has been kept in aqueous and also in an aqueous-alcoholic solution containing hydrofluoric acid; in the former case, carbon dioxide, alcohol, and sugar are formed during the first 24 hours, but with the mixture these products are not formed. Considerable differences are also met with in the amounts of nitrogenous substances left in the cells after remaining for ten days in contact with the two liquids. With pure water, the percentage of nitrogenous matter increases, but that of the carbohydrate decreases, and with the aqueous-alcoholic liquid the reverse is true. On the other hand, after ten days' maceration with water, the cells can no longer be distinguished, but after 30 months in the alcoholic liquid the cells keep their shape, the cell-wall becomes transparent, and granulations are visible in the interior.

Formaldehyde and amyl alcohol have been found among the products of autofermentation. The amounts are 38 milligrams of formaldehyde per 500 grams of yeast and 2 grams of amyl alcohol per kilogram of yeast.

J. J. S.

Photodynamic and Optical Behaviour of Anthraquinones. HERMANN VON TAPPEINER (*Chem. Centr.*, 1905, ii, 60—61; from *Arch. klin. Med.*, 82, 217—222).—[With A. JODLBAUER.]—The sulphonic acids of anthracene derivatives are very strongly fluorescent, and have been found also to have a very marked photodynamic action on *Paramæcia*, enzymes, and toxins. Experiments have now been made with derivatives of the anthraquinone series which do not show any visible fluorescence. In the experiments on *Paramæcia*, solutions of potassium anthraquinone-*a*-sulphonate, sodium anthraquinone-2:7-disulphonate, and sodium chrysophanate containing respectively 1 part in 500—20,000, 1 in 200—30,000, and 1 in 100,000—10,000,000, were used, whilst in the experiments on invertin, in addition to the salts of the above sulphonic acids, 0.05, 0.005, 0.01, and 0.1 per cent. solutions of sodium dichloroanthracenedisulphonate were also employed. Both anthraquinone-disulphonic acids were found to have a distinct photodynamic action,

and resembled the corresponding anthracene acids in this respect. The action of chrysophanic acid was still more marked, and was similar to that of dichloroanthracenedisulphonic acid.

The anthraquinonesulphonic acids had no effect on invertin in glass flasks, but a more concentrated solution of sodium anthraquinonedisulphonate, when exposed in uncovered dishes by an open window, was found to destroy entirely the activity of invertin.

[With HANS LEHMANN.]—Since it has been shown by measurements that members of the anthraquinone series do possess a distinct although a very faint fluorescence, the rule connecting fluorescence with photodynamic action still appears to hold. E. W. W.

Participation of Oxygen in the Action of Fluorescent Substances. A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1905, ii, 61—62; from *Arch. klin. Med.*, 82, 520—546. Compare Sacharow and Sachs, *Münch. med. Woch.*, 52, 297, and Pfeiffer, *Wien. klin. Woch.*, 18, 221 and 328).—Experiments on the action of sodium tetrabromotetraiodofluorescein (Rose-bengale), phenosafranine, and methylene-blue on *Proteus vulgaris*, and of erythrosine on enzymes and toxins (invertin, diastase, ricin), have shown that the effect of these fluorescent substances when exposed to light is dependent on the presence of oxygen. The compounds are inactive in the dark or in an atmosphere of hydrogen. The quantity of oxygen required is very small, and oxygen under pressure appears to have the same influence on photodynamic action. The fluorescent compounds, which had previously been found to have no action on invertin, were again tested in an atmosphere of oxygen. Quinine and harmaline almost entirely destroyed the activity of invertin in four days, whilst fluorescein had only about half the effect in the same time, and phenyl-2-methylquinoline had still less influence. Tolylene-red, Nile-blue, fluorenedisulphonic acid, and æsculin had no appreciable action in diffused daylight in four days or in sunlight in two days.

The photodynamic action on diastase in presence of oxygen did not cause the formation of more than an extremely small quantity of carbon dioxide, which was not detected with certainty, even when large quantities of the ferment were employed. The results of experiments in which so-called ozone reagents or readily oxidisable substances were used showed that oxidation did not take place, or was only very slight, even under the most favourable conditions. The change can only, therefore, be of a very limited extent, and must be due to a selective action on certain labile groups on which the specific action depends.

The decomposition of potassium iodide in diffused daylight is dependent on the presence of fluorescent compounds. Phenosafranine, azocarmine, and 4-phenyl-2-methylquinoline, and to a less extent α -naphtholtrisulphonic acid, β -naphthylaminedisulphonic acid, and naphthionic acid, which have a strong action on cells and enzymes, do not attack potassium iodide, or only very slightly, whilst on the other hand, in the case of fluorenedisulphonic acid or æsculin the reverse is true. The potassium iodide test is liable to error, and should only be used in conjunction with quantitative experiments on *Paramæcia* or enzymes. Straub's results (Abstr., 1904, i, 896) are ascribed to the

decomposition of the fluorescent substance in consequence of a bleaching action.

Eder's reaction between mercuric chloride and ammonium oxalate, which results in the formation of mercurous chloride, ammonium chloride, and carbon dioxide, is retarded by the presence of oxygen, but accelerated by the presence of fluorescent substances. The compounds of the fluorescein series, 4-phenyl-2-methylquinoline, quinine, acridine, anthraquinonedisulphonic acid, and dichloroanthracenedisulphonic acid, have been found to behave in this way, but methylene-blue, which is precipitated by Eder's solution, proved an exception. Non-fluorescent substances did not show this action. The inhibitive effect of oxygen is proportional to its partial pressure, and the action of light or of a fluorescent substance is greater in a vacuum or in an atmosphere which does not contain oxygen.

No explanation of these phenomena on the peroxide theory is feasible, but the formation of ions caused by the absorption of energy in the form of light is probably the cause of the action of fluorescent substances.

E. W. W.

Action of Liquid Air on the Life of Seeds. PAUL BECQUEREL (*Compt. rend.*, 1905, 140, 1652—1654).—The power of resistance of seeds towards low temperatures depends only on the amounts of water and gas present in their tissues. When a certain quantity of gas and water is present, the cold disorganises the protoplasm and the nucleus. If, however, the protoplasm has reached its maximum of concentration by drying, it completely escapes the action of low temperatures and does not freeze. The seed then retains its germinating power (compare Pictet and de Candolle, *Arch. Sci. phys. nat.*, 1895; Brown and Escombe, *Proc. Roy. Soc.*, 1895, 72, 161; and Dyer, *Abstr.*, 1900, ii, 300).

N. H. J. M.

Transformations of Nitrogenous Substances in Seeds during Maturation. GUSTAVE ANDRÉ (*Compt. rend.*, 1905, 140, 1417—1419. Compare *Abstr.*, 1904, ii, 634).—Vegetable albumin was not found in white lupin seeds at the commencement of their formation; when mature, the amount of nitrogen in this form was 2.5 per cent. of the total. Nitrogen in the form of legumin, also absent at the commencement, amounted to about 10 per cent. of the total at the same period. The nitrogen as soluble amides increased during maturation, and amounted at four different periods to 72, 81, 56, and 40 per cent. of the total nitrogen.

The transformations of nitrogen compounds during maturation of the seed are the reverse of those which take place during germination.

N. H. J. M.

Compound which yields Hydrogen Cyanide in Sambucus Nigra. GUIGNARD (*Compt. rend.*, 1905, 141, 16—20).—The greatest amount of hydrogen cyanide is obtained from the leaves, and there is no accumulation in the reserve organs. In this respect, *Sambucus* resembles *Lotus arabicus* and *Sorghum vulgare*. In the case of *Phaseolus lunatus*, the seed contains much glucoside.

N. H. J. M.

Presence of a Cyanogenetic Glucoside in the Leaves of *Sambucus Nigra*. ÉMILE BOURQUELOT and ÉMILE DANJON (*Compt. rend.*, 1905, 141, 59—61).—Leaves of *Sambucus nigra* contain a glucoside which, under the influence of emulsin, yields dextrose, hydrogen cyanide, and an aldehyde. The yield of hydrogen cyanide amounts to 0.126 gram from 1 kilogram of fresh leaves. N. H. J. M.

Simultaneous Variations of Organic Acids in some Oleaginous Plants. GUSTAVE ANDRÉ (*Compt. rend.*, 1905, 140, 1708—1711).—The amounts of soluble and insoluble oxalates in *Mesembryanthemum crystallinum* diminish as the age of the plant increases, whilst the malic acid increases. The sum of the oxalic and malic acids remains about the same (one-sixth of the dry matter). The ash of *M. crystallinum* contains a high percentage of potassium.

Sedum azureum, which contains more calcium than potassium, possesses very little total oxalate, and the soluble oxalates disappear completely before the plant dies. Malic acid is present at the commencement in considerable quantity and its amount does not change much during growth. N. H. J. M.

Carbohydrate Reserves of Evergreen Trees. LECLERC DU SABLON (*Compt. rend.*, 1905, 140, 1608—1610).—The maximum of reserve substances, which occurs in the autumn in the case of caducous leaves, is reached at the beginning of spring with evergreen plants. The minimum is in July or August. This explains why in evergreen trees assimilation is relatively feeble but continuous all the year round, whilst caducous leaves assimilate from May to October with much greater vigour. N. H. J. M.

Rhizomes of *Rheum palmatum* and *Rheum officinale* cultivated in Berne. ALEXANDER TSCHIRCH and P. A. A. F. ELJKEN (*Chem. Centr.*, 1905, ii, 144—145; from *Schweiz. Woch. Pharm.*, 1904, Nos. 40 and 41. Compare Abstr., 1903, i, 107; 1904, ii, 435).—The freshly cut surfaces of *Rheum palmatum* and *Rheum officinale* become strongly coloured on exposure to air, probably in consequence of the formation of gallic acid. Chrysophanic acid from *Rheum palmatum* melted at 162° and contained the methyl ester. By dissolving chrysophanic acid in ammonia and precipitating with acetic acid according to Hesse's method, a compound has been prepared which is either an amino-derivative or an ammonium salt; it crystallises from dilute acetic acid in dark brown, lustrous needles, melts above 260°, and is insoluble in ether but soluble in glacial acetic acid or in alcohol, forming a blood-red solution. The alcoholic solution is orange-red, but on the addition of alkalis or alkaline earths becomes red. *Amino-emodin* or *ammonia-emodin*, obtained by treating emodin with ammonia, forms a purplish-red powder which is insoluble in ether, but forms a cherry-red solution in alcohol. *isoEmodin*, $C_{15}H_{10}O_5$, has been isolated from the hydroxymethylanthraquinone by means of toluene; it sublimes in feathery crystals, melts at 212°, and is soluble in ether, alcohol, benzene, chloroform, glacial acetic acid, and in alkali hydroxides or

carbonates. Its solubility in hot toluene is greater than that of emodin. Ferric chloride gives a dark brown coloration with the alcoholic solution, and baryta and lime-water give flocculent, cherry-red precipitates. *iso*Emodin is probably identical with Hesse's rhabarberone. Rhein, $C_{15}H_8O_6$, crystallises from pyridine in bright yellow needles and melts at 314° ; diacetylrhein, $C_{15}H_8Ac_2O_6$, crystallises in bright yellow needles, and melts at $247-248^\circ$. *Amino-rhein* or *ammonia-rhein* is brown, and forms an orange-red solution in alcohol and a cherry-red solution in baryta water. Chrysophanic acid melting at 172° , *iso*emodin, and rhein have been isolated from the rhizomes of *Rheum officinale*, but not emodin. The roots contain the same compounds, but the presence of hydroxymethylantraquinone in the stalks, leaves, and fruit can only be detected by microscopical methods. The fresh rhizomes also contain an oxydase. *Rheum palmatum* contains more emodin than *Rheum officinale*, but the proportion of emodin to chrysophanic acid is much less in the latter. E. W. W.

Poisonous Action of Sodium Fluoride on Plants. OSCAR LOEW (*Chem. Centr.*, 1905, i, 1717—1718; from *Allg. bot. Zeit.*, 94, 330—338).—Sodium fluoride acts injuriously in two ways; it withdraws calcium from the plant and also acts like an alkaloid.

Some bacteria show a feeble development in 1 per cent. solutions of sodium fluoride; mould fungi will grow in 0.1 per cent. solutions.

N. H. J. M.

Action on the Soil of the Mineral Constituents of Plant Residues Soluble in Water. S. KRAWKOW (*J. Landw.*, 1905, 53, 279—288).—In accordance with results obtained by Schroeder and by Ramann, it was found that water percolating through leaves extracted considerable portions of the potassium, magnesium, sulphuric acid, and phosphoric acid, but very little of the calcium and silica. A good deal of the iron was also extracted.

When the water which had already percolated through leaves was allowed to percolate through soil, 58 per cent. of the potassium, 69 per cent. of the phosphoric acid, and 38 per cent. of the magnesium removed from the leaves was retained by the soil. On the other hand, the amounts of calcium and sulphuric acid showed a further increase after the water had percolated through the soil owing to the substitution of bases and to the action of the organic acids previously extracted from the leaves. The soil did not absorb appreciable amounts of sodium, iron, manganese, or silica.

N. H. J. M.

Water in the Soil and the Consumption of Water by Plants. CONRAD VON SEELHORST and MÜTHER (*J. Landw.*, 1905, 53, 239—259).—Experiments with oats and clover grown in boxes, on the consumption of water. The results are given fully in tables.

The fallow box lost nearly 6 grams of nitrogen, as nitrates, in nine months (June to February), the drainage containing on the average 24.6 per million of nitric nitrogen. The drainage amounted to 244 litres. The boxes with vegetation gave only 43.5, 44.6, and 30 litres respectively, containing 0.55, 0.49, and 1.18 gram of nitrogen. The greatest loss (1.18 grams) was in the clover box.

N. H. J. M.

Origin, Amount, and Importance of Carbon Dioxide in Soils. JULIUS STOKLASA and ADOLF ERNEST (*Centr. Bakt. Par.*, 1905, ii, 14, 723—736).—The carbon dioxide in soils is produced in the respiration of bacteria, moulds, algæ, and the roots of plants. The amount produced by microbes in 1 kilo. of arable soil (to a depth of 40 cm.) in 24 hours was from 17 to 50 mg. If only 15 mg. of carbon dioxide were produced in that time, the amount per hectare per annum would be 1400 kilos. when only 200 days of the year, on which an average temperature of 15° is reached, are counted. In the case of forest soil, the amount may be four times as great.

As regards the production of carbon by roots, 2,000,000 cereal plants (the minimal number per hectare) give off 60 kilos. per diem. Of the different plants included in the experiments, *Trifolium pratense*, *Beta vulgaris*, and *Avena sativa* produced the greatest amounts.

The action of roots, especially young roots, on the mineral substance of the soil is due to the carbon dioxide of the roots and not to organic acids, which, as Czapek (*Jahrb. wissens. Bot.*, 29) and Kossowitsch have shown, are not secreted by roots.

N. H. J. M.

Specific Action of Phosphoric Acid on Oat Plants grown in Black Moor Soil. H. CLAUSEN (*J. Landw.*, 1905, 53, 213—228).—The soil contains 8·2 per cent. of humus and 0·05 per cent. of calcium carbonate. The subsoil is yellow sand.

Application of phosphates increases the yield of oats, but diminishes the proportion of grain. The latter effect of phosphoric acid is less when the soil is dry and when aëration is increased.

Whilst the straw of the unmanured oats is pale yellow, that of the plants manured with superphosphate is bluish-red. Analysis of the ash of the plants shows that the former contains less calcium, but more than ten times as much iron as the latter. Calcium carbonate slightly increases both grain and straw, whilst basic slag somewhat reduces the yield of grain and considerably increases the straw.

N. H. J. M.

Analytical Chemistry.

Improvements in Gas Analysis Apparatus. ALFRED H. WHITE and EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1905, 27, 732—736).—An improved Hempel apparatus, the chief object of which is to prevent any chance of loss or gain in the volume of gas when transferring it to the burette or pipette. L. DE K.

Methods of Electro-analysis. NICOLAI A. PUSCHIN and R. M. TRECHZINSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 392—417).—The authors give the results of their investigations on the most suitable forms and arrangement of the apparatus in an electro-chemical labor-

atory. The paper does not admit of concise abstraction, but some of the more important points referred to are as follows.

In order to allow of the employment of a certain voltage as well as of a certain current density, the electrodes should be perforated plates, so arranged that the distance between them can be readily altered. The electrolytic cells should be tall parallelepipedal troughs of thin glass. In electro-analytical operations, both the voltage and the resistance should be exactly adjusted previously, and arrangements are described by which this can be rapidly effected, making use of Kohlrausch's alternating current and telephone method.

Contrary to what is indicated in electro-chemical text-books, the presence of a precipitate in the electrolytic liquid does not interfere with the electrolysis.

The advantages of using a rotating cathode or anode in conjunction with a high current density can be secured by the simpler device of keeping the solution in a state of vigorous agitation.

Designs are shown of simple switchboards for use in electro-chemical laboratories.

T. H. P.

Handling of Precipitates for Solution and Reprecipitation.

FRANK A. GOOCH (*Amer. J. Sci.*, 1905, [iv], 20, 11—12).—In case it is advisable to purify a precipitate by redissolving and reprecipitating the same, the author proposes to place within the filter a movable lining of platinum gauze on which the precipitate rests for the most part and with which it may be removed. The simplest plan is to cut a platinum gauze of such a shape that when folded it makes a cone of an angle a little less than 60° , and, holding it by pin-cers at the point of overlapping, it is placed within the filter and allowed to fit itself closely by the natural spring of the gauze when released. After the precipitate has been collected, the gauze is lifted out and immersed in a beaker containing the suitable solvent. The small amount of precipitate still adhering to the filter is readily removed by means of the wash-bottle. The final collection of the precipitate is of course made on the plain filter.

When using the Gooch perforated crucible, some precipitates are difficult to dissolve off the asbestos felt for the purpose of purification. In such cases, a disc of platinum perforated and provided with a wire handle is recommended.

L. DE K.

New Forms of [Analytical] Laboratory Apparatus.

CARL KIPPENBERGER (*Zeit. angew. Chem.*, 1905, 18, 1024—1025).—Improved apparatus, fully illustrated, for the determination of the saponification number, the estimation of volatile acids, alcohol, or ammonia by distillation, the testing of margarine and butter for sesamé oil, weighing flasks for milk and other liquids, and a pipette for measuring the amyl alcohol used in milk analysis.

L. DE K.

Use of Nickel Vessels in Laboratories. LOUIS L'HÔTE (*Ann. Chim. anal.*, 1905, 10, 253—254).—Nickel basins when electrolytically gold-plated and well polished may serve for evaporating strongly acid liquids. When nickel dishes or crucibles are heated in a muffle (such

as is used in sugar laboratories) until their weight has become constant, they may be used for milk analyses, including the estimation of the ash.

L. DE K.

Detection of the More Common Acids. STANLEY R. BENEDICT and JOHN F. SNELL (*J. Amer. Chem. Soc.*, 1905, 27, 736—744).—A systematic scheme for the detection of acids. The acids are separated as usual from the metals by boiling with a very strong solution of sodium carbonate, and should any copper have dissolved this is removed with hydrogen sulphide.

L. DE K.

Use of Sodium Peroxide in the Analysis of Organic Substances. II. HANS H. PRINGSHEIM and JAMES A. GIBSON (*Ber.*, 1905, 38, 2459—2461. Compare Pringsheim, *Abstr.*, 1904, ii, 447; Konek, *Abstr.*, 1903, ii, 572; 1904, ii, 588).—In order to avoid the filtration of large volumes of liquid, the reduction of the oxyhaloid salts formed by the action of sodium peroxide on organic substances containing halogens is now accomplished by the addition of sodium sulphite or sodium hydrogen sulphite and sulphuric acid; the contamination of the silver haloid with sulphate is avoided by adding 3 c.c. of concentrated nitric acid before the addition of silver nitrate.

G. Y.

Estimation of Sulphur and Phosphoric Acid in Foods, Fæces, and Urine. WILBUR L. DUBOIS (*J. Amer. Chem. Soc.*, 1905, 27, 729—732).—A modification of the method proposed by Neumann and Meinertz (this vol., ii, 59). Four grams of fresh foods, 2 grams of dried foods, or 1.5 grams of dried fæces are placed in a 100 c.c. nickel crucible, and when dealing with dry materials 2 c.c. of water are added. Five grams of anhydrous sodium carbonate are added, and then, gradually, 5 grams of sodium peroxide. The mass is dried very slowly over a low spirit flame, and then heated somewhat more strongly until it disintegrates and can be readily broken up into a powder. The charge is then covered with sodium peroxide and very gradually heated to bright redness. The phosphoric and sulphuric acids are estimated by the usual methods.

L. DE K.

Estimation of Sulphites by Iodine. R. HARMAN ASHLEY (*Amer. J. Sci.*, 1905, [iv], 20, 13—16. Compare this vol., ii, 351).—The author now states that it is possible to obtain good results in the titration of sulphites with iodine if the following conditions are adhered to.

One hundred c.c. of the sulphite solution containing one gram of sodium hydrogen carbonate are mixed with at least twice as much standard iodine solution as is required for complete oxidation. The liquid is then cautiously acidified with dilute hydrochloric acid (1:4), and the excess of iodine is titrated with standard sodium thiosulphate.

L. DE K.

Estimation of Ammonia in Potable Waters. JACQUES CAVALLIER and ARTUS (*Bull. Soc. chim.*, 1905, [iii], 33, 745—747).—Trillat and Turchel's method for detecting ammonia in water (*ibid.*, 1895, 13,

309) is of no special value for quantitative estimations. With the majority of waters, the method can be used only after considerable concentration, and even then the evanescent nature of the precipitate of nitrogen iodide renders the estimation difficult. J. J. S.

Free Acid in Superphosphate. LUDWIG SCHUCHT (*Zeit. angew. Chem.*, 1905, 18, 1020—1023).—Five grams of the sample are placed in a Buchner rapid filter sieve and extracted about ten times with acetone, using about 75 c.c. of this solvent altogether. The liquid, which becomes turbid owing to the presence of iron or aluminium phosphate, is rendered perfectly clear by addition of 200 c.c. of water, and after adding a little sodium oxalate and sodium chloride the free acid is titrated with $N/2$ alkali, using methyl-orange as indicator. If the sodium salts should cause a precipitate, this must first be filtered off. L. DE K.

Analysis of Graphitic Silicon and Siloxicon. PERCY E. SPIELMANN (*J. Soc. Chem. Ind.*, 1905, 24, 654—655).—Commercial [graphitic] silicon is best analysed by heating the powdered substance in a porcelain boat in a current of chlorine, when the silicon, iron, and aluminium volatilise as chlorides, leaving behind any silica or alumina. The temperature should be raised as high as possible towards the close of the operation. The gases are passed first over the surface of water contained in a flask and then through a U-tube loosely packed with wet cotton-wool; this absorbs the last traces of silicon chloride, and, after burning the wool, pure silica with only a trace of ferric oxide is left. The contents of the flask and the residue in the boat are then treated as usual.

Siloxicon.—This compound contains, according to an analysis by the author, 71.39 per cent. of $\text{Si}_2\text{C}_2\text{O}$, 10.81 per cent. of SiCO_3 , 5.81 per cent. of SiC , 10.06 per cent. of graphite, 1.07 per cent. of iron, and 0.86 per cent. of impurities. The total silicon may be readily estimated by fusing the substance with sodium peroxide and treating the mass, as usual, for silica. The total carbon may be estimated with sufficient accuracy by introducing small quantities of a mixture of siloxicon and sodium peroxide into a nickel crucible containing molten peroxide and then estimating the carbon dioxide thus produced by decomposition with dilute sulphuric acid and collecting the carbon dioxide in an ammoniacal solution of calcium chloride to form calcium carbonate. On heating the siloxicon in a current of chlorine, a portion of the silicon is expelled and may be collected as described. On igniting the residue in a current of oxygen, a portion of the carbon is oxidised and may be weighed in the usual manner, whilst the residue in the boat now consists of pure $\text{Si}_2\text{C}_2\text{O}$. The difference between the sum of total silicon, carbon, iron, moisture, and other impurities and the weight of the sample taken represents the oxygen. For minute details as to the calculation of the results, the original paper should be consulted. L. DE K.

Silicate Analysis. I. EDUARD JORDIS (*Zeit. anorg. Chem.*, 1905, 45, 362—367).—Attention is again called to the fact that although carefully conducted full analyses of silicates may give results closely

approaching 100 per cent., this is really due to a compensation of errors. For instance, the separated silica may retain alkalis and chlorine, whilst on the other hand the filtrate contains dissolved silica, which is, however, partly precipitated by ammonia in the presence of iron or aluminium. The solubility of the silica is increased by the presence of large quantities of calcium or alkali chlorides. The author also states that silica may retain free mineral acids, particularly sulphuric acid, at a red heat; these, however, may be expelled by repeated moistening with water and subsequent heating. Other errors may be caused by the use of inferior utensils or impure reagents. These errors may be reduced to a minimum by avoiding the use of porcelain dishes and of glass vessels which are not proof against acids or alkalis. Platinum dishes should be used for the evaporation of the acid silica solution. Care should be taken to use pure hydrochloric acid and the various reagents should all be freshly made with freshly distilled water.

L. DE K.

Expulsion of Ammonium Salts after Precipitation in their Presence. PAUL JANNASCH (*J. pr. Chem.*, 1905, [ii], 72, 38).—Large quantities of ammonium chloride are expelled from solutions by evaporation with concentrated nitric acid containing nitrous acid.

G. Y.

Electromotive Behaviour of Copper and Zinc in their Solutions in Potassium Cyanide. II. FRITZ SPITZER (*Zeit. Elektrochem.*, 1905, 11, 391—407. Compare this vol., ii, 501).—The electrolytic estimation of zinc and copper in solutions containing potassium cyanide is investigated. It is found that the platinum (or platinum-iridium) anode is attacked and the dissolved platinum deposited on the cathode. If this is allowed for, correct results can be obtained. The deposition of the metals is very slow owing to the fact that it only takes place as the cyanide is destroyed by oxidation at the anode, the last traces of metal being deposited from a solution practically free from cyanide. The oxidation takes place most rapidly in a $N/5$ alkaline solution. The presence of alkali hydroxide causes the deposition of some copper oxide at the anode. The presence of cyanide is therefore an unnecessary complication of the analysis, except in cases of separations; silver, for example, may be separated from copper electrolytically in presence of excess of potassium cyanide. Zinc is readily deposited in coherent form on a silvered platinum gauze cathode either from alkaline or faintly acid solutions (the latter containing excess of sodium acetate).

T. E.

Solubility of Copper Sulphide in Alkali Polysulphides. V. HASSEIDTER (*Zeit. angew. Chem.*, 1905, 18, 1023—1024).—A reply to the criticism of Rössing (*ibid.*, 465) regarding the author's statements as to the solubility of copper sulphide (this vol., ii, 285).

L. DE K.

Detection of Traces of Manganese in Presence of Iron in Well Waters. FR. CRONER (*Chem. Centr.*, 1905, ii, 74—75; from *Gesundh. Ing.*, 28, 197—198).—One hundred c.c. of the sample are

acidified with hydrochloric acid and filtered into a colorimeter 40 cm. high, 2 c.c. of a strong solution of tartaric acid are added, and then a slight excess of ammonia. On adding 2 c.c. of a saturated solution of potassium ferricyanide, a white turbidity is noticed either at once or after some time, according to the amount of manganese present. Traces of manganese may be identified in this manner.

L. DE K.

Separation of Iron from Manganese and Magnesium, and of Aluminium and Chromium from Manganese, Zinc, Nickel, and Magnesium by Hydroxylamine in Ammoniacal Solution. IV. PAUL JANNASCH and FRIEDRICH RÜHL (*J. pr. Chem.*, 1905, [ii], 72, 1—13. Compare Abstr., 1893, ii, 500; 1899, ii, 59; 1900, ii, 315; Jannasch and Mayer, this vol., ii, 557).—Iron may be quantitatively separated from manganese and magnesium by dissolving the substance to be analysed in hot dilute hydrochloric acid, adding 5—6 times its weight of hydroxylamine hydrochloride, and precipitating the iron by addition of concentrated ammonia to the hot solution. To ensure complete separation, it is necessary to dissolve the precipitate and repeat the precipitation in presence of about half as much hydroxylamine. If too much hydroxylamine is added, the precipitate is obtained in a finely-divided state and cannot be retained on the filter. On ignition, the precipitate, the composition of which has not been determined, yields a laminated residue of ferric oxide, which dissolves readily in hot concentrated hydrochloric acid.

In hydrochloric acid solution, chromates are reduced by hydroxylamine to chromium salts. Aluminium and chromium are quantitatively separated from manganese, zinc, nickel, and magnesium by a single precipitation with a slight excess of ammonia in presence of hydroxylamine; the precipitation is completed by warming on the water-bath. After evaporation of the filtrates and gentle ignition to expel ammonium and hydroxylamine salts, manganese, zinc, nickel, and magnesium may be estimated in the residue by the usual methods.

G. Y.

Quantitative Separations in Presence of Hydroxylamine. V. PAUL JANNASCH and WILHELM COHEN (*J. pr. Chem.*, 1905, [ii], 72, 14—26. Compare preceding abstract).—The precipitation of iron by ammonia in presence of hydroxylamine takes place normally in hydrobromic, hydriodic, sulphuric, or formic acid solutions; if much nitric acid is present, it must be neutralised, and the solution again acidified with a little hydrochloric acid. Organic acids, such as oxalic, citric, or tartaric acid, prevent complete precipitation; if the substance is dissolved in acetic acid, a small quantity of hydrochloric acid must be added before boiling with hydroxylamine, and after precipitation the solution may be again acidified with acetic acid. The precipitation of chromium and aluminium is effected similarly by the presence of different acids.

To separate aluminium or chromium from copper, the solution in water, or, if the chromium is present as chromate, in dilute hydrochloric acid, is boiled with hydroxylamine, excess of ammonia added,

and the solution warmed to complete precipitation; the precipitate must be well washed to free it from copper, which is estimated in the acidified filtrate by the ammonium thiocyanate method.

Iron is separated quantitatively from copper or zinc by boiling the solution in dilute hydrochloric acid with hydroxylamine until it appears colourless, and precipitating the iron by addition of ammonia to the boiling solution. The precipitate is washed, as far as possible, by decantation with boiling water, containing a little ammonia if zinc is present.

Before evaporating to dryness the filtrate containing zinc, the hydroxylamine must be decomposed by bromine water, as otherwise loss may occur owing to reduction of the zinc salt. G. Y.

Quantitative Separation of Iron and Thorium from Uranium by Hydroxylamine in Ammoniacal Solution VI. PAUL JANNASCH and JOHANNES SCHILLING (*J. pr. Chem.*, 1905, [ii], 72, 26—34. Compare preceding abstracts, and Abstr., 1899, ii, 59).—Iron and thorium are quantitatively separated from uranium by two precipitations by ammonia in presence of hydroxylamine salts. If the filtrate contains nitrates only, the uranium is estimated by evaporation to dryness and ignition; if other acids are present, the ammonium and hydroxylamine salts are expelled by gentle heating of the residue, or, after expulsion of the free ammonia by boiling, the hydroxylamine is decomposed by addition of bromine water, and the uranium precipitated with ammonia and weighed as U_3O_8 after ignition over the blow-pipe, and as UO_2 after ignition in a current of hydrogen.

With sodium acetate, thorium solutions yield slowly at the ordinary temperature, quickly on boiling, a granular, crystalline precipitate which is insoluble in excess of sodium acetate solution; the precipitation is not quantitative (compare Haber, Abstr., 1898, ii, 295). Thorium is precipitated partially from its solutions also by ammonium tartrate as a thick, white precipitate, and by tartaric acid as a voluminous, colloidal precipitate which is soluble in an excess of the reagent. Thorium is precipitated quantitatively from its solutions when boiled with ammonium, sodium, or potassium succinate.

G. Y.

Supplementary Remarks on the Hydroxylamine Method. PAUL JANNASCH (*J. pr. Chem.*, 1905, [ii], 72, 35—37. Compare preceding abstracts).—A discussion of the advantages of precipitation by ammonia in presence of hydroxylamine over other methods of quantitative separation.

The filtration of the iron precipitate takes place most easily if the precipitation is carried out at the ordinary temperature and the reaction mixture then heated on the water-bath for several hours.

G. Y.

A New Delicate Reagent for Nickel. LEO TSCHUGAEFF (*Ber.*, 1905, 38, 2520—2522).—An excess of ammonia or of sodium acetate is added to the solution to be tested for nickel and then a little powdered α -dimethylglyoxime, $OH \cdot N : CMe : CMe : N \cdot OH$. A scarlet precipitate is formed when the solution is boiled. The reaction is very

sensitive, definite results being obtained with solutions containing 1 part of nickel in 400,000 parts of water.

When cobalt is present, the solution is shaken with a large excess of ammonia before the dioxime is added.

The presence of 0.1 mg. of nickel in the presence of 500 mg. of cobalt can be distinctly recognised.

A convenient method for the preparation of dimethylglyoxime is described.
A. McK.

Test for Molybdenum. P. TRUCHOT (*Ann. Chim. anal.*, 1905, 10, 254).—As little as 0.01 mg. of molybdic acid may be recognised by heating the roasted substance with sulphuric acid in a porcelain crucible until only traces of free acid remain. When cold, the residue is breathed upon a few times, when, should molybdenum be present, a fine blue colour is developed. Should vanadium be also present, the colour will be more or less green.
L. DE K.

Separation of Tungsten Trioxide and Silicon Dioxide by means of Hydrogen Chloride and the Analysis of Silicotungstates. CARL FRIEDHEIM, W. H. HENDERSON, and ALFRED PINAGEL (*Zeit. anorg. Chem.*, 1905, 45, 396—409).—If hydrogen chloride is passed over a mixture of silicon dioxide, vanadium pentoxide, and tungsten trioxide at a cherry-red heat, the vanadium and tungsten pass over into the receiver (the vanadium partly in the quinquevalent, partly in the quadrivalent form; the tungsten only partially as trioxide); the silicon dioxide remains quantitatively in the platinum boat. The separation of the tungsten and vanadium is made after evaporation of the mixture with dilute sulphuric acid to which a little sulphurous acid has been added. The tungsten is weighed as trioxide; the vanadium is determined volumetrically by potassium permanganate.

In applying this hydrogen chloride method to ammonium salts, the material for analysis is freed from ammonia and water by heating, and the residue is then treated with hydrogen chloride as before. In dealing with potassium and sodium salts, special care must be taken to ensure that oxygen is absent from the hydrogen chloride, as it leads to the formation of chlorine, which attacks the crucible and causes unnecessary complication.

The original paper contains a careful comparison of the hydrogen chloride method with that of Marignac and others.
D. H. J.

Estimation of Titanic Acid in Minerals. P. TRUCHOT (*Chem. Centr.*, 1905, ii, 75; from *Rev. gen. Chim. pure appl.*, 8, 173—176).—A criticism of the various processes proposed from time to time. The following process is recommended. Two grams of the powdered mineral are fused with 12 grams of potassium-sodium carbonate and the mass is treated with cold water. The undissolved potassium titanate is dissolved in hydrochloric acid, neutralised with ammonia, again acidified with formic or acetic acid mixed with excess of sulphurous acid, and gently boiled for an hour. The precipitated oxide is then collected.
L. DE K.

Estimation and Separation of Thoria from the Oxides of the Yttrium-Cerium Group. WILLIAM B. GILES (*Chem. News*, 1905, 92, 1—3, 30—31).—The nitrates are dissolved in 100—200 times the amount of water, and the solution is saturated with hydrogen sulphide to reduce any ceric oxide to the cerous state. The liquid is then boiled to expel the gas, the volume of liquid being kept up by adding boiling water. When cold, a little freshly prepared moist lead carbonate of absolute purity is added, which, after acting for twelve hours with frequent stirring, completely precipitates the thoria and any zirconia, also any ferric oxide; uranic oxide, chromic oxide, and any alumina are but slowly and imperfectly precipitated.

Cerous oxide, lanthana, neodymia, praseodymia, yttria, samaria, and the members of the yttria group in general are not precipitated. After removing the excess of lead in the filtrate by means of hydrogen sulphide, they are separated as usual. The thorium precipitate is redissolved, freed from lead by means of hydrogen sulphide, and further treated by the usual method. If thought desirable, it may be subjected to a second treatment with lead carbonate. L. DE K.

Separation of Platinum and Iridium. L. QUENNESSEN (*Chem. News*, 1905, 92, 29—30).—After reviewing several processes, the author finally recommends the following process.

The alloy is dissolved in a mixture of one volume of nitric acid of sp. gr. 1.32 and two volumes of hydrochloric acid of sp. gr. 1.18, the liquid is evaporated to dryness and finally heated to 120° in an air-bath in order to expel completely the free nitric acid. The mass is then dissolved in water and the metals precipitated by means of metallic magnesium. The precipitate is dried and ignited and then heated to dull redness in a current of hydrogen. The mixture is treated with dilute sulphuric acid (1:10) to remove the excess of magnesium and then with dilute nitro-hydrochloric acid (1:3), which only dissolves the platinum; this is then recovered in the well-known manner by precipitation with ammonium chloride and ignition with addition of a little oxalic acid. If ignition is omitted before removing the magnesium with dilute sulphuric acid, the iridium is also dissolved. L. DE K.

Estimation of the Loss by Ignition in Soil Analysis. HEINRICH MEHRING (*J. Landw.*, 1905, 53, 229—237).—In order to restore to ignited calcium carbonate the whole of the carbon dioxide by treating with ammonium carbonate and drying at 150°, it is necessary to repeat the operation three times. In the case of soils containing carbonates it is impossible to obtain the correct weight in this manner. N. H. J. M.

Detection of Methyl Alcohol [in Ethyl Alcohol]. HEYWARD SCUDDER (*J. Amer. Chem. Soc.*, 1905, 27, 892—906).—A criticism of the various tests from time to time proposed. The following modification of the resorcinol test (*Abstr.*, 1899, ii, 388) is recommended when the amount of methyl alcohol falls below 2 per cent., and when only small quantities of the sample are available. Twenty-five c.c. of the sample are

fractionated through a Hempel tube made of glass tube 25.5 cm. long, 1.7 c.c. in diameter, filled with glass beads about 3 mm. in diameter. Three fractionations are made, the first time taking 15, then 7.5, and finally 2 c.c. One c.c. of the last fraction is diluted, oxidised by immersing in it several times a spiral of red hot copper wire, boiled down to half its bulk, and then tested for formaldehyde by the resorcinol test. If much formaldehyde is present, more or less abundant flocks will be noticed, but if there is but little only a contact ring will be visible.

If other substances should be present in the alcohol which might interfere with the test, these must be first removed by suitable means, such as distillation with acids or alkalis, &c.

L. DE K.

A Reagent for Phenols. JULES ALOY and F. LAPRADE (*Bull. Soc. chim.*, 1905, [iii], 33, 860—861).—The following solution serves as an extremely good reagent for phenolic substances. Dilute ammonium hydroxide is added to a solution of uranyl nitrate (10 grams) in water (60 c.c.) until a precipitate is just formed and the filtrate made up to 100 c.c. In testing for a phenol, 2 c.c. of the solution under examination are neutralised and the reagent added until no further coloration is produced. All phenols, simple or complex, with the exception of those containing numerous negative groups, for example, picric acid, give a red coloration. Mineral acids or alkalis destroy the colour.

J. J. S.

Estimation of Glycerol in Lyes. KARL BRAUN (*Chem. Zeit.*, 1905, 29, 763—765).—A review of the technical processes used for the determination of glycerol.

A modification of the dichromate process is proposed; 1 c.c. of the clarified lye is mixed with an excess of a strong solution of potassium dichromate, 10 c.c. of sulphuric acid are added, and the carbon dioxide generated on boiling is collected with the usual precautions in normal potassium hydroxide absolutely free from carbonate. The carbon dioxide is then precipitated with a hot solution of barium chloride, the precipitated barium carbonate is collected, washed until free from alkali, and then estimated volumetrically in the usual manner.

L. DE K.

Estimation of the Harmful Nitrogen in the Beet and in the Products of Sugar Factories. KARL ANDRÉK (*Zeit. Zuckerind. Böhm.*, 1905, 29, 513—518).—It has been shown by Herzfeld (*Zeit. Ver. Deut. Zuck. Ind.*, 1888, 38, 121) that a knowledge of the harmful nitrogen content is of great importance for the evaluation of the beet, and the author now gives the following simple method for estimating this nitrogen. One hundred grams of the beet pulp are weighed out and introduced into a flask holding 403 c.c., 3 c.c. being the volume of the washed and dried beet residue and precipitate. Water is added until the volume is about 340 c.c., and the flask heated for a quarter of an hour in a water-bath at 80—85°. Forty c.c. of a suspension of cupric hydroxide are then added, and 10 c.c. of aluminium sulphate solution (200 grams of the crystallised sulphate

per litre), the volume being then made up to about 408 c.c. and the flask well shaken. The flask is again heated at 80—85° for a quarter to half an hour and afterwards cooled, alcohol being added to bring the volume up to 403 c.c. In 100 c.c. of the clear filtrate, the following estimations are made: (1) total nitrogen by Kjeldahl's method, using sulphuric acid and a drop of mercury for the decolorisation; (2) ammonia- and amide-nitrogen, by boiling the 100 c.c. of liquid with 1 c.c. of concentrated sulphuric acid for two hours in a reflux apparatus, adding magnesia until the solution is alkaline to phenolphthalein, then a little paraffin, and distilling off the ammonia in the ordinary way. The difference between the two amounts of nitrogen thus obtained, when multiplied by four, gives the percentage of harmful nitrogen.

The filtrate from the copper precipitate is used also for the estimation of the sugar, 30—50 c.c. of the liquid being stirred up with 2—4 grams of zinc dust and filtered. The polarisation value of the solution multiplied by 1.042 gives the amount of sugar in the beet.

The molasses contain 1 part of harmful nitrogen per 25 to 27 parts of sugar. Ninety per cent. of the harmful nitrogen of the beet goes into the diffusion juice, and thence, in undiminished quantity, into the molasses. So that the harmful nitrogen is the main factor determining the proportion of molasses formed.

The cupric hydroxide used above for the precipitation of the proteid matter is prepared as follows: 200 grams of crystallised copper sulphate are dissolved in 10 litres of water and precipitated with sodium hydroxide solution; after the deposit has settled, the liquid is decanted away and the cupric hydroxide washed once by decantation with water. Twenty c.c. of glycerol are then added and the volume made up to 2 litres. The liquid can be kept for two months without appreciable change.

T. H. P.

Influence of the [Harmful] Nitrogen on the Purity of Sugar Syrup. KARL ANDRLÍK and J. URBAN (*Zeit. Zuckerind. Böhm.*, 1905, 29, 519—522).—The analysis of a large number of sugar syrups shows that a moderately regular relation exists between the purity coefficient and the content of harmful nitrogen, an increase in the latter causing a lowering of the former. With 1 part of harmful nitrogen corresponds from 15.1 to 17.7, or, on the average, 16.1 parts of non-saccharine material. This ratio of the harmful nitrogen to the total non-sugar of the syrup—to which the term "nitrogen-coefficient" is given—is regarded by the authors as a fairly constant magnitude, which undergoes but slight alterations in one and the same factory and during the whole of any one beet season.

The coefficient of purity, Q , of the syrup can be calculated from the expression $Q = \frac{10,000}{100 + K_N + N_s}$, where K_N is the nitrogen-coefficient and N_s the harmful nitrogen per 100 parts of sugar. In a number of syrups examined, the greatest difference between the calculated and actual coefficients of purity was found to be less than 0.7 per cent.

Knowing the amounts of sugar and harmful nitrogen present in a sample of beet, and assuming that 97 per cent. of the sugar and 90

per cent. of the harmful nitrogen pass into the diffusion syrup, the coefficient of purity of the saturated syrup can be calculated.

T. H. P.

Use of Fermentation Methods for the Analysis of Starch Syrup. ED. VON RAUMER (*Zeit. Nahr. Genussm.*, 1905, 9, 705—726).—By the use of pure yeast cultures, such as *Saccharomyces Marxianus*, which ferment dextrose, but not maltose, and have little action on dextrins, the author finds that ordinary starch syrup ("glucose") contains at least 13 per cent. of maltose. Where pure yeasts cannot be regularly obtained, bottom-fermentation beer yeast may be employed for the estimation of dextrins. The dextrin obtained from starch syrup is fermented or changed by the action of pressed yeast to the extent of about one-half, and the remainder is quite altered in its properties from the original dextrin.

W. P. S.

New Method of Milk Analysis. J. BELLIER (*Ann. Chim. anal.*, 1905, 10, 268—276).—Briefly, the process is as follows: a known weight of the sample is absorbed in a weighed piece of sponge, which is then dried at 80° and reweighed. The increase = total solids. The sponge is then extracted with ether; the loss = fat. The casein is then rendered insoluble by fumigating the sponge with formaldehyde vapour, and the lactose *plus* the bulk of the ash is extracted with 50 per cent. alcohol containing 5 per cent. of acetic acid. After washing with water, the sponge is again dried and the lactose found from the loss in weight, the casein being weighed directly.

The amount of ash retained by the casein may be taken as 0.01 per cent.; that extracted by the acid alcohol may be judged with sufficient accuracy by multiplying the non-fatty solids by 0.076; this factor only applies to cow's milk, and presupposes the absence of borates or other mineral salts.

L. DE K.

Estimation of Fat in [Milk, Condensed Milk, and Malted] Infant and Invalid Foods. C. B. COCHRAN (*J. Amer. Chem. Soc.*, 1905, 27, 906—909).—The apparatus consists of a flask furnished with a long, narrow, graduated neck, and also with a side-tube through which the liquids are introduced. Five c.c. of milk or 5 c.c. of condensed milk previously diluted (1:4) are introduced into the flask and mixed with 2.5 c.c. of 80 per cent. acetic acid, and then with 2.5 c.c. of strong sulphuric acid, and the flask is placed in hot water until the contents assume a coffee colour. When cold, 4 c.c. of ether are added, the whole is well shaken and then again placed in hot water until the ether has boiled off. Hot water is now introduced until the fat rises in the neck, where its volume is read off. The neck is so graduated that each division represents 0.1 per cent. of fat.

When dealing with infant or invalid foods, 1.72 grams of the sample are mixed with 5 c.c. of water and then analysed like milk; the result is multiplied by three. If an attempt is made to estimate the fat in such foods by direct extraction with light petroleum, only a very small fraction of the fat actually present is obtained.

L. DE K.

Use of Mineral Oil for the Determination of the Maumené Figure of Oils. FILIPPO SUZZI (*Chem. Centr.*, 1905, ii, 80—81; from *Boll. Chim. Farm.*, 44, 301—308).—When testing oils by Maumené's process (mixing with sulphuric acid and observing the rise in temperature), some oils become overheated and must be first suitably diluted with olive oil. Bishop and others have proposed the use of mineral oil, but the author cannot recommend this for drying oils. In the case of other oils, addition of mineral oil is permissible if the following formula is applied: $g = i/r \times v$, in which g is the desired Maumené's figure, i the observed rise in temperature, r the volume of the mixture minus the volume of the mineral oil, and v the total volume of the mixture.

L. DE K.

Optical Activity of the More Important Vegetable Oils. M. A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 442—451).—The author gives the results of measurements, by himself and others, of the sp. gr. and optical activity of 27 oils of vegetable origin.

T. H. P.

Optical Properties of Castor Oil, Cod-liver Oil, Neatsfoot Oil, and a Few Essential Oils. HERMANN C. LYTHGOE (*J. Amer. Chem. Soc.*, 1905, 27, 887—892).—A series of tables showing the refraction in the butyrefractometer at different temperatures of these oils. The sp. gr. and polarisation in the Ventzke apparatus is also given.

L. DE K.

Detection of Olive Oil which has been Extracted by means of Carbon Disulphide. GEORGES HALPHEN (*J. Pharm. Chim.*, 1905, [vi], 22, 54—56).—Although every effort is made by the manufacturers to remove all traces of carbon disulphide from olive oil which has been extracted by this solvent, some sulphur compounds always remain in the oil. These may be detected by saponifying the oil, salting out the soap by the addition of sodium chloride or sulphate, and testing the aqueous solution with silver nitrate. The thiosulphate yielded by all olive oils which have contained carbon disulphide gives a brown precipitate of silver sulphide. As pure olive oils themselves contain a small quantity of reducing substance which gives a faint brown coloration with silver nitrate, it is necessary to add a little copper sulphate to the soap solution before salting out. After adding the silver nitrate solution, the whole is acidified with acetic acid, boiled, cooled, and treated with an excess of ammonia. In this way, the test is rendered more delicate.

W. P. S.

Gasometric Estimation of Formaldehyde. GEORGE B. FRANKFORTER and RODNEY WEST (*J. Amer. Chem. Soc.*, 1905, 27, 714—719).—On adding 1 c.c. of formaldehyde solution to a mixture of 20 c.c. of normal potassium hydroxide, 25 c.c. of water, and 10 c.c. of hydrogen peroxide, one-half of the hydrogen from the aldehyde is liberated quantitatively, and when collected with the usual precautions its volume represents the formaldehyde contained in the sample.

Instead of a mixture of potassium hydroxide and hydrogen peroxide,

a solution of 2 grams of sodium peroxide in 50 c.c. of water may be employed, but the results are then liable to exceed the real amount slightly owing to liberation of oxygen by the action of the water on the peroxide.

L. DE K.

Estimation of Vanillin, Coumarin, and Acetanilide in Vanilla Extract. A. L. WINTON and E. MONROE BAILEY (*J. Amer. Chem. Soc.*, 1905, 27, 719—724. Compare Abstr., 1903, ii, 341).—A modification of the process recommended by Hess and Prescott. Twenty-five grams of the sample are diluted in a marked beaker to 50 c.c., evaporated at 70° to 25 c.c., again diluted to 50 c.c., and once more concentrated to 25 c.c. Normal lead acetate is added until no further precipitate forms, the precipitate is then collected and washed with hot water until the total filtrate amounts to 50 c.c. This, when cold, is shaken with 20 c.c. of ether, and the extraction is then repeated three times, using 15 c.c. of ether each time. The ethereal solution is shaken first with 10 c.c. of a 2 per cent. ammonia solution, and then three or four times in succession with 5 c.c. of the same. The ammoniacal extract contains the vanillin with traces of acetanilide. The ether is allowed to evaporate at the ordinary temperature, and the residue is dried in a desiccator and weighed. It is then extracted repeatedly with light petroleum (b. p. 30—40°), and the residue, after drying, is again weighed. It consists of acetanilide, and may be identified by the usual tests and its melting point. The petroleum, on evaporation, will leave any coumarin, also readily identified. The vanillin may be recovered from its ammoniacal solution by acidifying with hydrochloric acid and repeated agitation with ether. It is still liable to contain acetanilide, from which it may be freed by a second agitation with ether in the presence of ammonia. On evaporating the ether, the acetanilide remains.

L. DE K.

Micro-chemical Analysis of Cinchona Barks. P. VAN LEERSUM (*Chem. Centr.*, 1905, ii, 83; from *Pharm. Weekbl.*, 42, 432—435).—One milligram of the finely powdered bark is heated for a few minutes with 2 c.c. and then once more with 1 c.c. of benzene; the solution is evaporated to dryness and the residue dissolved in acetic acid. After evaporating, the residue is dissolved in water, and the solution is tested for quinine with sodium tartrate, potassium oxalate, and potassium chromate. It is as well also to apply the hercynic reaction, for which a weak solution of iodine and potassium iodide in a mixture of equal parts of water, alcohol, and acetic acid is used. When testing barks containing much of the inferior alkaloids, the quinine should be fractionally precipitated with sodium hydrogen carbonate and dissolved in ether.

L. DE K.

General and Physical Chemistry.

Magnetic Double Refraction of Sodium Vapour. J. GEEST (*Arch. Néerland.*, 1905, [ii], 10, 291—335).—The double refraction produced when a beam of light passes through sodium vapour in a strong magnetic field in a direction perpendicular to the lines of force has been examined and the phenomena registered photographically. Detailed observations relative to the quadruplet resulting from the ray D_1 , and the sextet resulting from D_2 , are recorded, and equations are developed on the basis of Voigt's theory which account for the complicated phenomena observed. H. M. D.

Charge carried by the α - and β -Rays of Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1905, [vi], 10, 193—208. Compare Abstr., 1904, ii, 799; this vol., ii, 218, 495).—In order to determine the charge carried by the α -particles, experiments were made with radium as nearly as possible in the condition of minimum activity, so as to avoid complications arising from the presence of β -particles. A known small quantity of radium bromide was dissolved in water and the solution evaporated uniformly on a polished aluminium or glass plate. The film of radium thus obtained was so thin (2.4×10^{-5} grams per sq. cm.) that only a very small fraction of the α -particles was absorbed by the radium itself. The saturation current due to the deposit thus obtained in the condition of minimum activity was measured between the radium-covered plate and a second plate placed above it at a distance of 3.5 cm., the electrodes being contained in a brass vessel in which a good vacuum was maintained by Dewar's charcoal absorption method. The apparatus was placed between the pole-pieces of a large electro-magnet so that the field was parallel to the plane of the plates, and the current was measured for various potential differences with and without the magnetic field, the radium-covered plate being in each case made positive and negative alternatively. When the magnetic field had attained a certain strength, the magnitude of the observed current was practically unaltered by further increase, indicating that the field was strong enough to prevent all the electrons from reaching the opposite plate. Assuming that each α -particle carries the same charge as an ion, then, from the value of the saturation current in the magnetic field and the known quantity of radium bromide employed, it is calculated that the total number of α -particles expelled per second from one gram of radium at its minimum activity is 6.2×10^{10} and in radioactive equilibrium four times as many, that is, 2.5×10^{11} (compare W. H. Bragg, this vol., ii, 4). In all probability the α -particles are already charged at the moment of expulsion.

Slow-speed electrons were emitted with the α -particles, and the current conveyed by these, as exemplified by the measurements without magnetic field, is sufficient to mask completely the current due to the α -particles. The fact that the current without magnetic field

is always greater when the radium-covered plate is negative than when it is positive shows that a greater number of electrons is emitted from this plate than from the other. The observations seem to indicate that these electrons constitute a type of secondary radiation resulting from the impact of α -particles on matter.

For the determination of the charge carried by the β -particles, a rod of lead, previously exposed to radium emanation until the excited activity had attained its maximum value, and wrapped in aluminium foil of thickness sufficient to absorb the α -rays completely, was suspended as the central electrode in a metal cylinder which was evacuated. The quantity of radium bromide corresponding with the γ -ray activity of the rod immediately after its removal from the emanation was first measured, and then in the above-mentioned apparatus the current due to the β -radiation was determined after a known time interval. From the known decay curve, this current was corrected to the original condition of the rod corresponding with the determined quantity of radium bromide. From the data, it is calculated that the number of β -particles expelled from one gram of radium per second is 7.3×10^{10} . This result, which is probably a little too high, is in agreement with the theory of successive changes, according to which four α -particles are expelled from radium in radioactive equilibrium for each β -particle.

From the calculated number of α -particles expelled per gram per second, several other constants are deduced. Assuming that only one α -particle is expelled during the disintegration of the radium atom, it follows that in a gram of radium about 0.5 milligram disintegrates per year. The time required for half transformation of the radium is 1280 years, and the average life of radium is 1850 years. Assuming that each atom of radium gives rise to one atom of emanation, the maximum volume of emanation obtainable from one gram of radium in equilibrium is 0.83 c.mm. (Ramsay and Soddy found experimentally about 1 c.mm.).

From the previously determined kinetic energy of the α -particle = 5.9×10^{-6} erg, the emission of energy in gram calories per gram per hour is calculated to be 126 (Curie and Laborde found 100 by experiment).

The average number of ions produced by each α -particle in air at atmospheric pressure is calculated to be 86,000, or, since the range of the particle is 3 cm., the number of ions per centimetre of path in air at normal pressure is 29,000. The ionising power of the α -particles appears to be about twice as great as that of electrons.

Finally, the average energy required to produce an ion is calculated to be 2.7×10^{-11} ergs.

H. M. D.

Action of Radium Emanations on Minerals and Gems.
CHARLES BASKERVILLE and L. B. LOCKHART (*Amer. J. Sci.*, 1905, [iv], 20, 95—96).—The emanation from 0.25 gram of radium chloride, 7000 uranies strong (one uranie being the radioactivity of metallic uranium), was allowed to act on various minerals at the temperature of liquid air. Wollastonite, willemite, greenockite, and tiffanyite were found to glow strongly. Kunzite, which is very responsive to

radium, exhibited no fluorescence or phosphorescence when the emanations were condensed; it is therefore responsive to the β - and γ -rays only. Pectolite and spodumene did not glow.

It was also observed that zinc sulphide does not glow when cooled to the temperature of liquid air, either with or without exhaustion of the air. Similarly, no effect is observed when zinc sulphide in a vacuum is suddenly subjected to atmospheric pressure, but when warmed to the ordinary temperature, after being cooled by means of liquid air, it glows brilliantly.

H. M. D.

Radiotellurium and Polonium. WILLY MARCKWALD (*Jahrb. Radioaktiv. Elektronik.*, 1905, 2, 133—136. Compare this vol., ii, 159).—The opinion expressed by Debierne (Abstr., 1904, ii, 642) that no distinction can be drawn between radiotellurium and polonium is not supported by the experimental data. The decay curves of different specimens of polonium prepared by Mme. Curie indicate that several radioactive constituents are present. On the other hand, independent determinations of the rate of decay of radiotellurium have given the same constant, and there can be little doubt as to its individual and specific character.

H. M. D.

Radioactivity Constant of Radiotellurium. WILLY MARCKWALD, H. GREINACHER, and K. HERRMANN (*Jahrb. Radioaktiv. Elektronik.*, 1905, 2, 136—139).—The radioactivity at different times was obtained by measurement of the saturation current between two strips of silver, on one of which the radiotellurium had been deposited, the quantity being less than 0.001 milligram. The electrodes, about 2 mm. apart, were sealed into a glass tube, and the times required for charging a condenser of known capacity to a given potential by the saturation current were measured. The experimental data satisfy the logarithmic equation $I_t = I_0 e^{-\lambda t}$. The radioactive constant is 0.00497 day, or 57.4×10^{-9} seconds. The activity falls to half value in 139.6 days, and the average life of radiotellurium is 201.2 days.

H. M. D.

Decay of the Radioactivity of Radiotellurium. H. GREINACHER (*Jahrb. Radioaktiv. Elektronik.*, 1905, 2, 139—142).—Similar experiments (compare preceding abstract) were made with a specimen of radiotellurium deposited two years previously on a strip of copper. The observed rate of decay is expressible by means of the same constant as that of the freshly deposited radiotellurium. Working with a constant difference of potential, it was found that when the distance between the electrodes is gradually increased, the current at first increases, attains a maximum, and then decreases. As the decay of the radioactivity proceeds, the distance to which the electrodes must be separated to obtain the maximum current gradually increases.

H. M. D.

Gases produced by Actinium. ANDRE DEBIERNE (*Compt. rend.*, 1905, 141, 383—385. Compare Abstr., 1904, ii, 223, 729).—The gas evolved by a solution of actinium chloride in water was examined by

Ramsay and Soddy's method and shown to consist of hydrogen, oxygen, and helium. The amount of helium produced is similar to that yielded by radium, although the amount of emanation furnished by actinium is very small. The disengagement of helium from solid actinium fluoride, dried at 200° , was also observed. In some cases, the gas obtained from the solid salt gave an intense continuous spectrum in which hydrogen and mercury lines showed faintly. The nature of the gas producing this spectrum has not yet been determined. T. A. H.

Phosphorescence of Zinc Sulphide through the Influence of Condensed Gases obtained by Heating Rare-earth Minerals. CHARLES BASKERVILLE and L. B. LOCKHART (*Amer. J. Sci.*, 1905, [iv], 20, 93—94).—A large number of minerals containing thorium and uranium and several artificial uranium compounds were ignited, the evolved gases condensed, and their effect on phosphorescent zinc sulphide was observed. Although no very definite conclusion could be drawn from the experiments, it appeared that those minerals which afford the largest quantities of helium give the greatest amounts of emanation. The detailed observations are recorded. H. M. D.

Supposed Radioactivity of Hydrogen Peroxide. MAURICE PADOA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 43—44).—The author shows that the action of hydrogen peroxide at a distance on a photographic plate cannot be due to any form of radiation, but is caused by the emission from the peroxide of vapours capable of diffusing unchanged through various substances. If platinum black or manganese dioxide, which is capable of decomposing hydrogen peroxide, is inserted between the peroxide and the photographic plate, no action takes place. T. H. P.

Electrical Conductivity and Absorptive Power for Heat Radiations of Metallic Sulphides and Oxides occurring Naturally. JOHANN KOENIGSBERGER and O. REICHENHEIM (*Centr. Min.*, 1905, 454—470. Compare Hagen and Rubens, *Abstr.*, 1903, ii, 348).—Quantitative determinations were made of the electrical conductivity and of the absorptive and reflective powers for heat radiations of the following minerals: hæmatite, marcasite, pyrites, molybdenite, stibnite, galena, chalcocite, and graphite. The results are in agreement with Maxwell's equation $n^2\kappa = \sigma\tau$, where n is the index of refraction, κ that of absorption, σ the absolute conductivity of the substance, and τ the period of the electromagnetic vibration. L. J. S.

Liquid Dielectrics. P. GOURÉ DE VILLEMONTÉE (*Compt. rend.*, 1905, 141, 179—181).—Two cylindrical condensers are employed filled respectively with petroleum and with paraffin oil; the outer coating is raised to a potential V , the inner being connected to earth; the inner coating is then connected with the electrometer and the outer to earth, and the change on the inner measured. It is found, if p be the charge and t the time of charging, that $\log p/Vt$ is a linear function of $\log t$. In the next experiments, the inner cylinder was

connected directly with an electrometer, the outer being at potential V , and it was found that the charge, in equal time, is proportional to the potential V . A curve is also given expressing the effect of time. The liquid itself is found to acquire no charge. L. M. J.

Limiting Conductivity of certain Binary Electrolytes in Acetone. PAUL DUTOIT and ALEX. LEVIER (*J. Chim. Phys.*, 1905, 3, 435—454. Compare Carrara, Abstr., 1897, ii, 471; Laszczynski, Abstr., 1896, ii, 556).—The authors have investigated the cause of the lack of agreement in the results obtained for the conductivity of acetone solutions by previous investigators. The measurements were made with the bromides, iodides, and thiocyanates of lithium, sodium, potassium, and ammonium, carefully purified acetone having a specific conductivity $0.5\text{--}2.0 \times 10^{-7}$ (Siemens unit) being employed as solvent.

Concordant values can only be obtained when unplatinised electrodes are used, the dissolved electrolyte being absorbed to an appreciable extent by platinum black. Errors may also result in consequence of changes of the solute and of the presence of very small quantities of impurities in the solvent. For instance, the conductivity of ammonium salts varies with the time, and in the case of lithium thiocyanate very different results are obtained with different specimens of the salt.

The following numbers, obtained by interpolation, represent the values of the molecular conductivity at 18° (Siemens units):—

V .	250.	500.	1000.	2000.	5000.	10,000.	20,000.	50,000.	100,000.	∞ .
LiBr	47.0	65.0	82.0	99.5	120.5	133.0	142.0	150.5	154.0	155.0
NaBr	73.0	88.0	104.9	120.2	136.5	145.0	150.9	157.2	158.0	158.0
KBr	—	—	—	126.5	139.0	147.0	152.5	155.5	—	155.5
NH ₄ Br	—	49.2	61.4	77.5	100.3	118.6	135.7	153.0	157.0	157.5
LiI	—	113.0	125.6	135.8	145.4	150.1	154.0	157.0	157.0	157.0
NaI	—	121.0	130.6	139.8	148.8	152.4	155.0	155.5	155.5	155.5
KI	—	127.3	136.8	143.1	150.7	155.0	157.0	157.5	157.5	157.5
NH ₄ I	—	95.4	110.5	126.5	142.0	150.0	155.1	157.0	157.5	157.5
NaCNS	91.5	107.0	122.0	137.5	151.0	—	—	—	—	(169)
KCNS	113.4	126.7	139.0	148.5	158.5	163.5	167.5	170.0	170.0	170.0
NH ₄ CNS ...	66	83	102	122	144	157	166	170	171	171

In all cases the molecular conductivity increases with the dilution and approximates to a limiting value. The limiting values satisfy the law of Kohlrausch, but the ratio of the ionic velocities is different from that in water. From the limiting conductivity values the degree of dissociation of the various electrolytes has been calculated. The dissociation of the corresponding salts increases in the series: ammonium, lithium, sodium, potassium, and in the series: chloride, bromide, thiocyanate, iodide. The extent of the dissociation appears thus to depend in an additive manner on the component ions.

H. M. D.

Effect caused by Heating the Cathode of the Silver Voltameter to Redness on the Value of the Electrochemical Equivalent. G. VAN DIJK (*Arch. Néerland.*, 1905, [ii], 10, 277—283. Compare Abstr., 1904, ii, 255).—The author's experiments indicate that no measurable quantity of solution is enclosed by the

deposited silver except when the deposition takes place on a layer of the metal deposited previously which has been heated to redness, whereby probably small fissures and cavities are produced in consequence of unequal expansion of the silver layer and the containing platinum vessel. The true value of the electrochemical equivalent of silver is given as 0.011180.

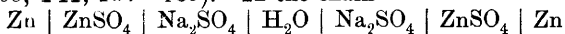
H. M. D.

Deposition of Alloys from Mixed Solutions. CHARLES B. JACOBS (*J. Amer. Chem. Soc.*, 1905, 27, 972—976).—The following method has been devised for the simultaneous deposition of zinc and nickel. Neutral solutions of zinc and nickel sulphates were used in the bath, and varying proportions of ammonium sulphate and chloride were added in order to regulate the internal resistance. The anodes employed were of zinc and nickel respectively. In order to maintain the proper difference in voltage between the two anodes and the cathode, two generators were used running at different voltages, that at the higher voltage for the zinc, and that at the lower voltage for the nickel anode, the current returning through the cathode by a common third lead to the generators. The anodes were arranged on each side of the revolving cathode at distances which could be varied, and it was thus possible to determine the voltage which, in relation to the internal resistance of the bath, would give the desired proportions of zinc and nickel in the deposit.

Some experiments were made on a small scale on the simultaneous deposition of copper and zinc from a solution of their sulphates, and a product resembling yellow brass was obtained. Better results were obtained with a cyanide solution, a copper anode being used on the low voltage side and a zinc anode on the high voltage side, and it was found that the colour of the brass could be easily regulated by varying the voltage on either side.

E. G.

Effect of Membranes in Liquid Chains. M. CHANOTZ (*Compt. rend.*, 1905, 141, 184—185).—In the chain



with symmetrical concentrations, one $\text{Na}_2\text{SO}_4 \mid \text{H}_2\text{O}$ contact is made by means of a membrane of animal parchment, when an *E.M.F.* is produced, and the Na_2SO_4 becomes negative. The difference of potential is affected by the relative positions of the solution and water and other causes which can be all traced to diffusion effects. If $N/100$ H_2SO_4 replaces the Na_2SO_4 , the difference of potential is in the reverse sense, and in all cases it varies with the nature of the membrane.

L. M. J.

Determination of Melting Point. ANTON LANDSIEDL (*Chem. Zeit.*, 1905, 29, 765—766).—The author describes an apparatus for the determination of melting points. The thermometer is fixed in a tube by a cork through which passes also a long capillary lying close to the stem of the thermometer, and having a constriction opposite the bulb of the latter. Through this permanent capillary the successive melting-point tubes may be slipped down until they lie close to the bulb of the thermometer. The tube containing the thermometer and capillary is immersed for a considerable portion of its length in

sulphuric acid, so that the melting points determined are to be regarded as corrected. The tube containing the sulphuric acid is protected by gauze, asbestos paper, and a glass cylinder, so that the loss of heat to the air is a minimum, and melting points up to 310° can be determined without trouble. J. C. P.

New Apparatus for the Determination of Melting Points.

MAURICE DE THIERRY (*Arch. Sci. phys. nat.*, 1905, [iv], 20, 59—61).—The author describes a form of apparatus in which the solid is placed between two contact poles in an electric circuit, which form contact when the solid melts. If the substance is itself a conductor, it is enclosed in a small, thin glass tube with a pointed end, and forms the upper contact pole; owing to the restriction at the end, no contact is made until the solid melts. L. M. J.

Melting Point of Gold and Expansion of some Gases at High Temperatures. I. ADRIEN JACQUEROD and F. LOUIS PERROT (*Arch. Sci. phys. nat.*, 1905, [iv], 20, 28—58).—The present paper contains chiefly the account of the apparatus and method of procedure. The gold is in the form of a thin wire, which forms part of an electric circuit that is broken when the wire melts. It is heated in a platinum resistance furnace about 300 mm. long and 50 mm. in diameter, 58 turns of platinum wire, 0.7 mm. in diameter, being employed. The gas thermometer is constructed of fused silica, which possesses many advantages over platinum-iridium (Holborn and Day, *Abstr.*, 1901, ii, 84), notably an extremely low coefficient of expansion (0.00000162), which is very constant up to 1000° . To test the apparatus and thermometer, the boiling point of naphthalene was determined, the thermometer being filled with hydrogen; the value found was 215.8° , agreeing well with the previous determination, 215.64° . To determine the variation of temperature in different parts of the furnace, the apparent melting point of a gold wire placed in different parts was determined. Within the distance over which the thermometer bulb extended, the differences from the value at the middle point (1066.9°) only reached 1.8° ; near the end of the furnace, the difference reached 8° . L. M. J.

State of Matter in the Neighbourhood of the Critical Point.

GABRIEL BERTRAND and JEAN LECARME (*Compt. rend.*, 1905, 141, 320—323).—When a closed tube, freed from air and containing less than one-third of its volume of a solution of alizarin in alcohol, is heated, the solvent volatilises completely below the critical point, leaving the alizarin as a solid deposit. When a tube containing more than one-third of its volume of this solution is heated, the meniscus disappears at a temperature a little higher than the critical point of the solvent, the tube becomes filled with a fluid showing striæ, and the dye gradually diffuses uniformly throughout the fluid, and this condition continues even if the temperature be raised 20° above the critical point.

A solution of potassium dichromate in water behaves similarly, but

the phenomenon is more difficult to exhibit in this case because of the fracture of the tubes as a result of the high pressure developed.

These observations afford further evidence in favour of the view taken by Ramsay (Abstr., 1881, 971; 1882, 136, 267; Jamin, *ibid.*, 1883, 898; Cailletet and Colardeau, *ibid.*, 1891, 779), that a substance exists simultaneously in the gaseous and liquid states at its critical point, and even at temperatures slightly above this (compare Andrews, Trans., 1870, 23, 74).

T. A. H.

State of Matter in the Neighbourhood of the Critical Point. C. RAVEAU (*Compt. rend.*, 1905, 141, 348—349).—The author is of opinion that Bertrand and Lecarme (preceding abstract) are not justified in assuming that because the vapour of alcohol at a temperature below the critical point does not dissolve alizarin, it does not do so at or just above the critical point, since, as is well known, there is a rapid change in the properties of fluids in the immediate neighbourhood of the critical state.

T. A. H.

Parr's Method for Estimating the Heat of Combustion. GEORG LUNGE and HERMANN GROSSMANN (*Zeit. angew. Chem.*, 1905, 18, 1249—1253).—Parr's method for determining the heat of combustion of coal is suitable for ordinary coals, but unsuitable for brown coals. A finely powdered mixture of 0.5 gram of coal, 0.5 gram of tartaric acid, and 10 grams of sodium peroxide of good quality is used for the estimation.

A. McK.

Thermochemistry of Phenylhydrazones. PH. LANDRIEU (*Compt. rend.*, 1905, 141, 358—361).—The amounts of heat developed in the formation of phenylhydrazones in aqueous, alcoholic, or ethereal solution, as was most convenient, were determined experimentally, and, using existing data as to heats of formation of the various ketones and aldehydes and of phenylhydrazine, the heats of formation of the phenylhydrazones were calculated and compared with those deduced from the heats of combustion of the phenylhydrazones as determined in the calorimetric bomb. The results obtained for the phenylhydrazones of the following compounds by the two methods were respectively as follows: acetone, 45.9 and 44.9 Cal.; acetaldehyde, 40.0 and 39.1 Cal.; benzaldehyde, 11.6 and 10.1 Cal.; furfuraldehyde, 36.1 and 34.0 Cal.; salicylaldehyde, 43.6 and 41.7 Cal.; and anisaldehyde, 38.5 and 35.1 Cal. The reactions of benzophenone and acetophenone with phenylhydrazine do not take place quickly enough to be suitable for calorimetric measurement. The heats of formation of the phenylhydrazones of these two ketones were therefore deduced from their heats of combustion only, the results obtained being -10.1 Cal. and 19.4 Cal. respectively.

The amount of heat developed in the action of phenylhydrazine on aldehydes or ketones is, as a rule, from 12 to 16 Cal., and is slightly greater than that (10 to 13 Cal.) developed in the action of hydroxylamine on these substances (this vol., ii, 301).

T. A. H.

Dissociation of Carbon Dioxide. WALTHER NERNST and H. VON WARTENBERG (*Chem. Centr.*, 1905, ii, 314; from *Nachr. k. Ges. Wiss. Göttingen*, 1905, 64—74).—The apparatus and methods used in investigating the dissociation of carbon dioxide resemble those previously employed in the case of water vapour (*Nachr. k. Ges. Wiss. Göttingen*, 1905, 35—45). The results of the experiments show that the catalytic action of the capillary tube through which the gases escape varies very greatly with different tubes. The range of temperature in which the dissociation is sufficiently great and the reaction velocity of the capillary sufficiently small is limited. The capillary tube must therefore be narrow. Since moisture also acts as a catalytic agent, the gas requires to be carefully dried. The results are arranged in a table in the original paper, and are also shown graphically by means of two curves. The initial portion of the upper curve, which corresponds with the formation of carbon dioxide, appears to represent a termolecular reaction. It is found, however, that the data are affected by a unimolecular reaction. The lower curve, which represents a bimolecular reaction, is also affected by the unimolecular reaction, especially in the neighbourhood of the equilibrium point. The equilibrium value x_0 , when the combination of carbon monoxide with oxygen is regarded as unipolar, is 0.029. The value of x at 1300°, calculated from Hahn's data, is 0.00419 per cent.; thermodynamical calculations give 0.00400 at 1300°, 0.0138 at 1400°, and 0.032 at 1478°.

E. W. W.

Apparatus for Measuring the Absolute Coefficient of Internal Friction of Gases. SILVIO CHELLA (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 23—30).—Coulomb's method for the absolute measurement of the coefficient of internal friction of gases presents great difficulty when the influence of the rim of the oscillating disc is to be taken accurately into account. For the purpose of overcoming this disadvantage, the author has devised an apparatus in which the disc is replaced by a cylindrical bell; by varying the density of the latter, it is possible to keep the diameter constant whilst the weight and moment of inertia change. The apparatus is described and depicted, and the corresponding formula for the coefficient derived.

T. H. P.

Nature of Osmotic Pressure. ANGELO BATELLI and ANNIBALE STEFANINI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 3—14).—The authors bring forward a modification of Traube's theory of osmotic pressure, according to which osmotic phenomena are always determined by the difference between the surface tensions of the two liquids, but the direction of osmosis is always that tending to equalise the surface tensions on the two sides of the diaphragm. With water and alcohol, for example, if the diaphragm is impermeable to alcohol, the water alone passes through; whilst if it is permeable to both liquids, flow takes place in both directions. In the latter case, that direction of flow is favoured with which the change of surface tension is relatively the greater. Solutions having equal surface tensions, although not equimolecular, are always in osmotic equilibrium. It

is hence improbable that osmotic pressure is of a purely kinetic nature, as van't Hoff's theory supposes.

Nernst's derivation of formulæ for *E.M.F.* from osmotic pressure is no proof of the validity of the osmotic theory, since it has been shown by Helmholtz that the formulæ can be arrived at in quite another way.

T. H. P.

Velocity of Crystallisation of Supersaturated Solutions. CH. LEENHARDT (*Compt. rend.*, 1905, 141, 188—189).—The author has obtained in the case of the crystallisation of supersaturated solutions results similar to those obtained by Tammann for supercooled liquids. Thus, in the case of sodium acetate, which melts in its water of crystallisation at 58°, the velocity of crystallisation increases to about 25°, after which it remains constant to about -20°, falling very rapidly below this temperature to become inappreciable at about -40°. In the case of sodium thiosulphate, the effect of addition of the anhydrous salt was also studied, the results being stated to prove that the diminution of the velocity is proportional to the square root of the quantity of anhydrous salt.

L. M. J.

Catalytic Ester Exchanges. I. Contribution to the Theory of Saponification. ROBERT KREMANN (*Monatsh.*, 1905, 26, 783—822. Compare this vol., ii, 307; Skraup, *Abstr.*, 1894, i, 15; Skraup and Fortner, *Abstr.*, 1894, i, 404).—In alcoholic solution at 60°, ethyl mucate is completely hydrolysed in 2—3 minutes by a slight excess of 0.2*N* alcoholic sodium hydroxide. If an alcoholic solution of tetra-acetylmucic acid is treated with 10 per cent. less alcoholic sodium hydroxide than is necessary for complete hydrolysis and neutralisation of the carboxyl groups, it immediately yields sodium mucate, and 78 per cent. of the acetyl present is converted into ethyl acetate, the hydrolysis of which by the remaining alcoholic sodium hydroxide takes place only extremely slowly. With the amount of sodium hydroxide necessary for complete hydrolysis in alcoholic solution, ethyl tetra-acetylmucate yields about 65 per cent. of its acetyl as ethyl acetate. The yield of ethyl acetate from tetra-acetylmucic acid decreases rapidly with diminution of the amount of sodium hydroxide; with ethyl tetra-acetylmucate, the decrease is not so rapid. The formation of ethyl acetate must be due to instantaneous splitting off of the acetyl groups without consumption of sodium hydroxide. The reaction with ethyl tetra-acetylmucate is complicated by the formation of by-products, due probably to intermediate lactone formation, which takes place to a small extent if the hydrolysis is carried out at higher temperatures and in more dilute solutions.

A similar formation of ethyl or methyl acetate takes place when the acetates of polyhydric or of higher molecular monohydric alcohols, such as amyl acetate, are treated with sodium hydroxide in ethyl- or methyl-alcoholic solution. In alcoholic solution at 60°, with 5, 3, and 7 per cent. of the respective amounts of sodium hydroxide necessary for complete hydrolysis, glycol diacetate, triacetin, and mannitol hexaacetate yield immediately 93, 86, and 88 per cent. of the theoretical amounts of ethyl acetate. The yield of ethyl acetate is not increased

by the addition of larger amounts up to 94 per cent. of the theoretical quantity of sodium hydroxide, and the reaction will take place with as little as 1 per cent. of sodium hydroxide, but in that case the maximum yield of ethyl acetate is obtained only after some minutes. The rate of formation of ethyl acetate from triacetin, as determined in a series of experiments in alcoholic solution at 25°, and with 0.29, 0.58, 1.46, and 2.91 per cent. of the theoretical amount of sodium hydroxide, was found to vary with, but not strictly in proportion to, the percentage of sodium hydroxide present.

The formation of methyl acetate from triacetin in the presence of sodium hydroxide in methyl-alcoholic solution is more rapid than that of ethyl acetate in ethyl-alcoholic solution; further, ethyl acetate is formed more rapidly from glycol diacetate than from triacetin. Ethyl acetate and glycol are formed from glycol diacetate and ethyl alcohol, even in absence of sodium hydroxide.

The author considers that these "ester exchanges" are due to the formation of an equilibrium between the acetate dissolved and the acetate of the alcohol functioning as the solvent; this takes place extremely slowly owing to the small concentration of the ions (compare Euler, Abstr., 1901, ii, 376), but is greatly accelerated by the addition of the more strongly dissociating sodium alkoxide. G. Y.

New Form of Pyknometer. R. V. STANFORD (*Phil. Mag.*, 1905, [vi], 10, 269—270).—The pyknometer is bottle-shaped, the neck terminating in a short vertical capillary. The second capillary is sealed into the body of the pyknometer a short distance below the neck, and for the greater part of its length is horizontal; near its extremity, however, the capillary is bent at right angles, so that the top is vertical. By means of a small plunger, which can be connected to the longer capillary by means of india-rubber tubing, the liquid meniscus can be brought to a mark on the horizontal portion of the tube. The pyknometer rests without support on a stand in the thermostat, and wire suspension is dispensed with. H. M. D.

New Fractionating Tap. A. VON BARTAL (*Chem. Zeit.*, 1905, 29, 786—787).—The tap has four horizontal tubes radiating from it, three of which, *B*, *C*, *D*, are at a lower level than the remaining one, *A*. The stopper has a horizontal groove cut completely round it at the level of the tube *A*; from the horizontal groove, a small vertical one is cut extending to the level of the other three tubes. By a slight turn of the stopper the tube *A* can be put successively into connection with either of the tubes *B*, *C*, or *D*, or can be completely shut off from them all. P. H.

Tap for Use with Alkaline Liquids. LASSAR-COHN (*Chem. Zeit.*, 1905, 29, 901—902).—The body and side-tubes of the tap are constructed of glass, whilst the stopper is made of phosphor-bronze; between the metallic stopper and the glass body is inserted a layer of rubber. P. H.

Condensers with Ball Mouth-piece. FRITZ HINDEN (*Chem. Zeit.*, 1905, 29, 809—810).—A conically elongated ball mouth-piece takes the place of the usual cork. It may be placed on various distilling flasks and even on suitable beakers. A number of illustrations are given. It is shown that the joint so formed is sufficiently tight for practical purposes.

L. DE K.

Inorganic Chemistry.

Chemical Oxydases. G. BAUDRAN (*Compt. rend.*, 1905, **141**, 330—331. Compare this vol., ii, 407).—Chlorine, bromine, iodine, and iodine trichloride each give a red colour even in very dilute aqueous solutions with “guaiacol water” (Bertrand’s reagent). They likewise destroy the toxicity of alkaloids and toxins. The alkali and alkaline earth salts of the halogen acids are also active, the latter being slightly the more powerful. These actions are inhibited by the presence of phenol.

T. A. H.

Methods employed in Preparing the Tables of Specific Gravity of Sulphuric, Nitric, and Hydrochloric Acids and Ammonia. W. C. FERGUSON (*J. Soc. Chem. Ind.*, 1905, **24**, 781—790).—The tables have been based on C.P. compounds. All specific gravity determinations were taken at 60° F. compared with water at 60° F. The thermometer employed was readable to 1/18° F., and was frequently checked against a standard thermometer; the accuracy of balance and weights was also systematically checked against standard weights. The effect due to expansion of the pyknometer was found to be so small as to be negligible. The strength of the standard sulphuric acid was determined by titration against standard solutions of sodium carbonate (prepared by heating to 572° F. and by igniting to constant weight), ammonium sulphate, 100 per cent. sulphuric acid (prepared by crystallisation), sulphuric anhydride, and sulphanilic acid; the results obtained varied between the limits 97.40 and 97.415 per cent., leaving out of account one value of 97.34. The caustic soda solution was prepared from C.P. caustic soda purified by baryta, and was titrated against the acid, using methyl-orange as indicator, the same substance being employed as indicator in titrating the nitric and hydrochloric acids as well as the ammonia. The nitric acid the constants of which were to be determined was free from nitrous and hydrochloric acids, and the hydrochloric acid contained only traces of impurities which would affect the determinations less than the errors of manipulation. The ammonia was prepared from C.P. ammonia by distilling it with lime into distilled water. The sulphuric acid used had sp. gr. 1.84; it was free from hydrochloric and nitric acids and ammonium salts. For further details of the methods employed, as well as for the tables of numerical results, reference should be made to the original paper.

P. H.

Phosphorus Subiodide and the Role of this Substance in the Allotropic Transformation of Phosphorus. R. BOULOUCH (*Compt. rend.*, 1905, 141, 256—258).—When dry iodine is added to a solution of phosphorus in dry carbon disulphide in quantity less than is necessary to convert the phosphorus into the di-iodide, and the mixture is exposed to sunlight, *phosphorus subiodide*, P_4I , separates. This is an amorphous, red powder, it decomposes without melting, forming phosphorus di-iodide (which dissociates) and phosphorus vapour, and is only slowly attacked by water. Dilute nitric acid attacks the subiodide vigorously, liberating iodine, and with concentrated nitric acid it inflames. Concentrated solutions of the alkali hydroxides dissolve it, liberating hydrogen phosphide, and dilute solutions of the alkali hydroxides or carbonates convert it into "Leverrier's suboxide," P_4OH (compare Gautier, this Journal, 1873, 352). Phosphorus subiodide dissolves in solutions of iodine forming phosphorus di-iodide or tri-iodide; this reaction serves to distinguish it from red phosphorus.

The catalytic conversion of yellow into red phosphorus by the agency of iodine is explained by assuming that phosphorus di-iodide is first formed, and this, in contact with excess of phosphorus, is converted into phosphorus subiodide, which at temperatures above 160° undergoes a series of decompositions resulting in the formation of phosphorus di-iodide, which immediately dissociates, and red phosphorus. This explanation of the allotropic transformation is similar to that proposed by Brodie (this Journal, 1852, 5, 289), and regarded as unacceptable by Hittorf.

T. A. H.

Preparation of Vitreous Arsenious Oxide. LORENZ SOUHEUR (D.R.-P. 159541).—Arsenious oxide is usually converted into the vitreous form by distillation or by fusion under pressure. It is found that the application of pressure alone is sufficient to effect the conversion, which is accelerated by heating to a temperature below the melting point. Thus a pressure of 2500 kilograms per sq. cm. converts arsenious acid at 150° completely into the vitreous modification.

C. H. D.

Influence of Water Vapour on the Reduction of Carbon Dioxide by Carbon. OCTAVE BOUDOUARD (*Compt. rend.*, 1905, 141, 252—253. Compare this vol., ii, 91).—"Dry" and "moist" carbon dioxide were passed over purified wood charcoal contained in a porcelain tube heated at temperatures varying from 650° to 1000° . At 800° , the reduction of carbon dioxide took place more rapidly in the moist than in the dry mixture, but the difference rapidly disappeared as the temperature was increased, and at 1000° the rapidity of action was the same whether the gas was dry or moist. The rate at which the current of gas was passed had little influence on the action. These observations indicate that the greater rapidity of reaction which attends the use of dry air in the blast furnace is the direct result of the difference in hygrometric state, and is not due to the dryness of the air favouring the formation of carbon monoxide.

T. A. H.

Causticising [of Potassium Carbonate]. GUIDO BODLÄNDER and R. LUCAS (*Zeit. angew. Chem.*, 1905, 18, 1137—1141).—The action $K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH$ is reversible; the action for technical purposes is more complete when carried out in dilute solution, although the necessity of the subsequent concentration involves an expenditure of heat.

The solubility of lime in solutions of sodium hydroxide of varying concentrations was estimated at 50°. The ratio $(OH)^2/CO_3$ was determined with solutions of lime in a mixture of potassium hydroxide and potassium carbonate of varying concentrations at 18° and at 25° respectively. Determinations of the ratio $(OH)^2/CO_3$ are also quoted where barium hydroxide and strontium hydroxide respectively were substituted for lime. A. McK.

Preparation of Double Silicates of Potassium with other Bases. ANDRE G. DUBOIN (*Compt. rend.*, 1905, 141, 254—256. Compare Abstr., 1895, ii, 351 and 1897, ii, 96).—When silica is projected into melted potassium fluoride contained in a platinum crucible, and to this molten liquid precipitated zinc oxide is added, and the mass produced on cooling is re-melted with the addition of potassium chloride, and maintained in a molten condition for 72 hours, two *potassium zinc silicates* are formed, which may be separated by washing with a heavy liquid prepared by dissolving mercuric iodide in solution of lithium or sodium iodide in water (this vol., ii, 637). One of these silicates forms small, prismatic crystals, has a sp. gr. 3.68 at 0°, and the composition represented by the formula $K_2O, 6ZnO, 4SiO_2$; the other occurs in large, prismatic crystals, has a sp. gr. 2.96 at 0°, and the composition represented by the formula $8K_2O, 9ZnO, 17SiO_2$. Both are readily decomposed by hydrochloric acid. These silicates are not analogous in constitution with the potassium magnesium silicates similarly produced (*loc. cit.*). T. A. H.

Crystallisation of Sodium Iodide from Alcohols. MORRIS LOEB (*J. Amer. Chem. Soc.*, 1905, 27, 1019—1020).—Sodium iodide separates from methyl alcohol in plates or needles having the composition $NaI, 3CH_3 \cdot OH$, whilst from ethyl alcohol it crystallises as $NaI, C_2H_5 \cdot OH$. *n*-Propyl alcohol dissolves about one-third of its weight of sodium iodide, and the solution deposits crystals of the composition $5NaI, 3C_3H_7 \cdot OH$. Potassium iodide separates from an alcoholic solution in crystals which do not contain any of the solvent. E. G.

Compounds of Sodium with Zinc. C. H. MATHEWSON (*Zeit. anorg. Chem.*, 1905, 46, 94—112).—A complete fusion diagram has been constructed according to Tammann's methods. The melting-point curve consists of six branches; there are two well-marked maxima at 477° and 27.92 per cent. of sodium, and 576° and 16.23 per cent. of sodium respectively. Five distinct compounds of zinc and sodium exist, namely: (1) Na_4Sn , which at 405° undergoes transformation according to the equation $Na_4Sn \rightleftharpoons 0.091 Na_2Sn + \text{fused alloy} (3.82 \text{ mols.})$

Na + 0.91 mol. Sn). (2) Na_2Sn , with a melting point of 477° . (3) Na_4Sn_3 ; it is the hardest and most brittle of the five compounds. At 478° , it melts with transformation according to the equation $\text{Na}_4\text{Sn}_3 \rightleftharpoons 0.375 \text{ NaSn} + \text{fused alloy}$ (3.62 mols. Na + 2.62 mols. Sn). It occurs in two crystalline modifications, α and β ; the transformation of the β into the α -crystals is attended by considerable increase of volume. (4) NaSn , with a melting point of 576° ; at 483° , it undergoes a polymorphous transformation. (5) NaSn_2 ; it is the softest and toughest of the five compounds, and, like NaSn , has the appearance of tin. At 305° , it undergoes transformation in accordance with the equation $\text{NaSn}_2 \rightleftharpoons 0.667 \text{ NaSn} + \text{fused alloy}$ (0.333 mol. Na + 1.333 mols. Sn). The easy oxidation of the alloys prevented their examination under the microscope. A freshly cut surface of Na_4Sn or Na_2Sn soon becomes covered in the air with a bronze film, but under vaseline the surface of the former resembles that of tin, whilst the latter is steel-blue. Na_4Sn_3 shows a pale blue colour on a fresh surface; no film colour appears on oxidation. D. H. J.

Silver-aluminium Alloys. G. I. PETRENKO (*Zeit. anorg. Chem.*, 1905, **46**, 49—59).—From the complete fusion diagram constructed by Tammann's method, it is clear that two distinct compounds of aluminium and silver exist, namely, AlAg_2 and AlAg_3 . The melting-point curve falls from the melting point of aluminium to the eutectic point at 567° , then rises to the melting point of silver; on the rising point of the curve are two breaks, at 721° and 11.15 per cent. Al, 771° and 7.72 per cent. Al respectively, corresponding with the two compounds mentioned. Both compounds exist in two polymorphous forms.

The alloys with from 7.72 to 11.3 per cent. of aluminium take a good polish; those with from 0 to 7.72 per cent. of Al are quite stable in the air. D. H. J.

Calcium Chloroborates. LEON OUVARD (*Compt. rend.*, 1905, **141**, 351—354. Compare Rousseau and Allaire, *Abstr.*, 1893, ii, 468, 518; 1894, ii, 413, 447; and Ouvard, 1900, ii, 206, 207; 1901, ii, 158).—The following salts are prepared by fusing together boric anhydride and calcium chloride in various proportions, given in detail in the original, with or without the addition of lime.

The salt $3\text{CaO}, \text{CaCl}_2, 5\text{B}_2\text{O}_3$ crystallises in needles or prisms showing longitudinal extinction, is scarcely soluble in water or dilute acetic acid, but readily so in dilute mineral acids. The compound $3\text{CaO}, \text{CaCl}_2, 3\text{B}_2\text{O}_3$ forms arborescent masses of granular crystals, which are feebly active towards polarised light and are rendered opaque by water. There is simultaneously formed with this a calcium borate having the formula $2\text{CaO}, \text{B}_2\text{O}_3$, crystallising in lamellæ, which are very active towards polarised light and insoluble in water, but soluble in dilute acids.

Le Chatelier's calcium chloroborate, $3\text{CaO}, \text{CaCl}_2, \text{B}_2\text{O}_3$ (*Abstr.*, 1884, 1261), and the calcium borate having the formula $3\text{CaO}, \text{B}_2\text{O}_3$ were also prepared. T. A. H.

Behaviour of Typical Hydrated Bromides when Heated in an Atmosphere of Hydrogen Bromide. J. LEHN KREIDER (*Amer. J. Sci.*, 1905, [iv], 20, 97—106).—The hydrated bromides of barium, magnesium, and aluminium were heated at different temperatures for half an hour in a current of dry air and in a current of hydrogen bromide, and the loss of water and of hydrogen bromide was determined in each case. The dehydration of barium bromide, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$, at 70 — 160° takes place without any appreciable loss of hydrogen bromide, whether heated in air or in a current of hydrogen bromide, and the rate of dehydration is approximately the same in the two cases. In the dehydration of magnesium bromide, $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, approximately a third of the water may be removed without any considerable loss of hydrogen bromide. From this point, the loss of hydrogen bromide, when the salt is heated in air, increases with the temperature and is inhibited, as is the loss of water, by an atmosphere of hydrogen bromide. From this, the conclusion is drawn that two molecules of water bear a different relationship to the salt from the other four molecules. Hydrated aluminium bromide, $\text{AlBr}_3 \cdot 6\text{H}_2\text{O}$, when heated at 100 — 210° , loses water and hydrogen bromide simultaneously both in air and in an atmosphere of hydrogen bromide, but the loss of water as well as of hydrogen bromide is retarded in the latter case. A differentiation of the water molecules in aluminium bromide is, however, not indicated by the experimental data. Formulæ for the hydrates in accordance with Cushmann's hypothesis of inner and outer leakages of water are suggested to account for the observed phenomena.
H. M. D.

Magnalium and other Light Alloys. ROBERT E. BARNETT (*J. Soc. Chem. Ind.*, 1905, 24, 832—834).—Magnalium, which is the name given to an alloy of aluminium with magnesium, is manufactured in three varieties, X, Y, and Z. The alloy has a greater tendency to oxidation when hot than aluminium, but its advantages over that metal are its much greater tensile strength, and the fact that it is much better adapted to turning, &c. The following analyses were obtained from the various samples, most of the aluminium hydroxide being removed by digestion with sodium hydroxide before proceeding to the separation of the other metals. Alloy X contains copper, 1.76; magnesium, 1.60; nickel, 1.16 per cent., and antimony and iron in smaller quantities. Alloy Y, which appears to be intermediate in composition between X and Z except as regards nickel, contains copper, magnesium, tin, lead, a small amount of iron, and a doubtful trace of antimony. Alloy Z (soft sheet) contains tin, 3.15; copper, 0.21; magnesium, 1.58; lead, 0.72 per cent., and about 0.3 per cent. of iron. Zisium, sp. gr. 2.95, and ziskon, sp. gr. 3.35, are two silver-white alloys which are used in scientific instrument making. Zisium is essentially aluminium with small amounts of zinc, tin, copper, and traces of antimony and bismuth. Ziskon is a zinc-aluminium alloy, containing 25 per cent. of the former metal.
P. H.

Alloys of Magnesium with Tin and Thallium. GEORG GRUBE (*Zeit. anorg. Chem.*, 1905, 46, 76—93).—The alloys have been studied

by the fusion method of Tammann, and the results have been confirmed by microscopic examination.

I. Magnesium-tin Alloys.—The melting-point curve falls from the melting point of magnesium to a eutectic point corresponding with the temperature 564.8° and 39 per cent. of tin; it then rises to a maximum point at 783.4° and 70.95 per cent. of tin. From the maximum point, which indicates the existence of the definite compound, SnMg_2 , it falls to a second eutectic point at 209.4° and 97.5 per cent. of tin, and finally rises to the melting point of tin. SnMg_2 is formed with considerable development of heat on melting together its constituents in hydrogen at $700\text{--}800^{\circ}$; it crystallises well, is brittle, and easily tarnishes in the air.

II. Magnesium-thallium Alloys.—The melting-point curve falls from the melting point of magnesium to a eutectic point corresponding with 403.7° and 72.5 per cent. of thallium. It next rises to a maximum at 76 per cent. and 412.9° . From this maximum it falls to a second eutectic point at 392.9° and 84.8 per cent. of thallium, and then to further eutectic points at 355.4° and 89.3 per cent. of thallium and at 205.2° and 97.1 per cent. of thallium, and finally rises to the melting point of thallium. From the course of the curve, with its sharp maximum and two concealed maxima, the existence of three compounds is inferred, namely, Tl_3Mg_8 , TlMg_3 , and Tl_2Mg_3 . Tl_3Mg_8 melts at 412.9° to a homogeneous liquid. TlMg_2 undergoes transformation at 392.9° in accordance with the equation $\text{TlMg}_2 \rightleftharpoons 0.0796 \text{ Tl}_3\text{Mg}_8 + \text{fused alloy } (0.9204 \text{ Tl} + 1.9204 \text{ Mg})$. Tl_2Mg_3 has a transformation point at 355.4° : $\text{Tl}_2\text{Mg}_3 \rightleftharpoons 0.1194 \text{ TlMg}_2 + \text{fused alloy } (1.8806 \text{ Tl} + 2.8806 \text{ Mg})$. Thallium-magnesium alloys blacken in the air by oxidation, especially in presence of moisture. D. H. J.

Heavy Liquids containing Alkali Mercuric Iodides. ANDRÉ G. DUBOIN (*Compt. rend.*, 1905, 141, 385—388).—These liquids are prepared by adding mercuric iodide and the appropriate alkali iodide alternately to a small quantity of water until this is saturated. The solution of potassium mercuric iodide has a sp. gr. 3.196 at 22.9° and $n=1.730$ at 26° ; that of sodium mercuric iodide has sp. gr. 3.46 at 26° and $n=1.797$; that of lithium mercuric iodide a sp. gr. 3.28 at 25.6° and $n=1.783$, and the preparation of ammonium mercuric iodide a sp. gr. 2.98 at 26° and $n=1.527$.

These liquids are sensitive to atmospheric conditions. Those containing sodium or lithium give a precipitate of mercuric iodide with water, but are soluble in alcohol. The ammonium mercuric iodide solution deposits crystals having the composition $2\text{NH}_4\text{I} \cdot \text{HgI}_2 \cdot \text{H}_2\text{O}$. The solutions containing ammonium or potassium iodide give precipitates with the other two solutions. The sodium mercuric iodide solution is soluble in a variety of organic solvents. Cellulose swells and becomes transparent when placed in this liquid, and the product, after being washed with a solution of sodium iodide in water, dries to a horny mass. T. A. H.

Different States of Oxidation of Aluminium Powder. ÉMILE KOHN-ABREST (*Compt. rend.*, 1905, 141, 323—324. Compare Abstr., 1904, ii, 261).—When aluminium powder is heated in a current of air,

it begins to absorb oxygen at 400° ; between 400° and 625° , the rate of absorption increases steadily and remains constant between 625° and 750° . At 800° , a further absorption of oxygen commences, which increases as the temperature is raised to 1000° , and then remains constant between 1000° and 1200° .

When aluminium powder is heated during one hour at 1000° or for the same period at temperatures rising from 500° to 1050° , 59 per cent. of oxygen is absorbed, and no further absorption of oxygen occurs when the heating is continued for another two hours at 1000° . The product is a homogeneous pearl-grey powder, which decomposes hydrochloric acid with effervescence.

It is pointed out that the formation of a suboxide AlO would require the absorption of nearly 59 per cent. of oxygen. The results of other experiments, to be described later, indicate the possible existence of oxides of the formulæ Al_4O_3 and Al_2O (compare Pionchon, *Abstr.*, 1893, ii, 572).

T. A. H.

Mechanical Properties of Iron in Isolated Crystals. FLORIS OSMOND and CH. FRÉMONT (*Compt. rend.*, 1905, 141, 361—363).—A number of nearly pure iron crystals, some of which measured several c.c. in volume, were isolated from a portion of a steel rail and subjected to tension, compression, hardness, and bending tests. Descriptions of the special methods of applying these tests and the numerical results obtained are given. The results show that the mechanical properties of isolated crystals of iron are a function of the crystallographic orientation in its relation to the direction in which the stress is applied. The material is very brittle in the directions of the planes of cleavage, but shows great plasticity in other directions.

T. A. H.

Absorption Spectrum of Manganous Salts. P. LAMBERT (*Compt. rend.*, 1905, 141, 357—358).—A specimen of manganous chloride, prepared from carefully purified manganese dioxide, gave an absorption spectrum having the following bands: (1) an intense broad band between $\lambda = 513.0$ and $\lambda = 557.5$, (2) a broad, less intense band between $\lambda = 420$ and $\lambda = 442.50$, and (3) a group of six narrow bands occupying the following positions: (a) $\lambda = 410.25$ to $\lambda = 412.25$, (b) $\lambda = 405.25$ to $\lambda = 408$, (c) $\lambda = 402$ to $\lambda = 403.25$, (d) $\lambda = 400$ to $\lambda = 401$, (e) $\lambda = 396.25$ to $\lambda = 397.75$, and (f) $\lambda = 394.5$ to $\lambda = 395.75$.

T. A. H.

Influence of Nitrogen on Iron and Steel. HJALMAR BRAUNE (*Rev. de Métallurgie*, 1905, 2, 497—502).—When iron is heated at 800° in an atmosphere of ammonia, iron nitride is produced, forming a solid solution with iron, lowering its melting point, and lessening its power of dissolving carbon. The nitride may be caused to diffuse equally through the iron by subsequent annealing. The size of the ferrite crystals diminishes as the percentage of nitrogen increases, and at 0.20 per cent. of nitrogen the cellular structure of the ferrite disappears, a system of linear markings appearing. The tensile strength of iron

increases with the proportion of nitrogen, the ductility falling rapidly. The magnetic coercive force and hysteresis are greatly increased.

Steel containing 1.15 per cent. of carbon becomes brittle with 0.040—0.045 per cent. of nitrogen. In the case of quenched steels, the nitride remains in solid solution in the martensite. C. H. D.

Effect of Nitrogen on Steel. HENRI LE CHATELIER (*Rev. de Métallurgie*, 1905, 2, 503—507).—Braune's discovery (preceding abstract) of the influence of nitrogen on iron and steel explains the difference in fragility often observed between steels of identical composition. Iron does not combine directly with atmospheric nitrogen, the presence of a basic slag and of reducing agents is necessary; it is therefore chiefly in the blast-furnace and in the basic converter that absorption of nitrogen takes place, probably through the formation of cyanides. Furnaces producing much potassium cyanide are known to yield an inferior quality of iron.

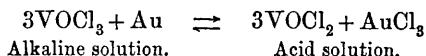
The linear markings observed in ferrite crystals containing nitrogen are identical with Neumann's lines, and are probably due to twinning, which takes place more readily in iron nitride during polishing than in pure ferrite. C. H. D.

Variations of Basicity in Chromium Salts. ALBERT COLSON (*Compt. rend.*, 1905, 141, 331—333).—To explain the inertness of chromium pentasulphate, $\text{Cr}_4\text{O}(\text{SO}_4)_5$ (this vol., ii, 94), towards reagents, it is suggested that the light green hydrated oxide precipitated from violet chrome alum has the constitution $\text{O}:\text{Cr}_2(\text{OH})_4$. In conformity with this view, the oxide (1 mol.) dissolves in cold dilute acetic acid (6 mols.), yielding a violet-coloured solution in which a *tetra-acetate*, $\text{O}:\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 2\text{H}_2\text{O}$, exists, which is obtained in the form of amorphous spangles. The chromic oxide is not readily displaced from this salt by potassium hydroxide, and on the addition of potassium hydroxide to aqueous solutions of the tetra-acetate, precipitation takes place only after several days at 0° , after some hours at 20° , and in a few minutes at 60° (compare this vol., ii, 460). It is suggested that on the addition of potassium hydroxide a soluble compound of the type $\text{O}:\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_2\text{O}_2\text{K}_2$ is formed, two molecules of which then interact, yielding potassium acetate and chromic oxide, represented by the formula $\text{O}:\text{Cr}_2 \begin{smallmatrix} \text{O}_2 \\ \text{O}_2 \end{smallmatrix} \text{Cr}_2:\text{O}$. This precipitate is dark green and is less basic than the light green product similarly precipitated from chrome alum, which, when shaken with a solution of an alkali sulphate, liberates the alkali so that the solution shows an alkaline reaction with phenolphthalein or reddened litmus (compare this vol., ii, 34).

T. A. H.

Behaviour of Vanadium Compounds towards Metallic Gold and Gold Solutions. FRANZ HUNDESHAGEN (*Chem. Zeit.*, 1905, 29, 799—800).—Vanadic acid and other vanadic compounds do not precipitate gold from either acid neutral or alkaline solutions; in hydrochloric acid solution or in presence of chlorides they exert a solvent action on gold, becoming thereby reduced to the vanadous or hypo-

vanadous condition ; if the solution is then made neutral or alkaline, the whole of the gold is at once precipitated as a greyish-violet powder which redissolves again on acidifying the solution. This reaction may be represented thus :



Selenic and telluric acids behave in the same way. These facts have some bearing on the deposition and solution of gold in nature.

The following is suggested as a ready test for vanadic acid in minerals: the powdered mineral, added to concentrated hydrochloric acid on a white porcelain basin, develops an orange-brown coloration of vanadium chloride, which is easily distinguished from the olive-brown produced by manganese dioxide. P. H.

Gold-tin Alloys. RUDOLF VOGEL (*Zeit. anorg. Chem.*, 1905, 46, 60—75).—A complete fusion diagram has been constructed according to Tamman's methods, and the results deduced have been confirmed by a microscopic investigation. For purposes of comparison, a figure is also given in which are included curves showing the results of the fusion experiments together with (1) the curve of electrical conductivity (Matthiessen), (2) the curve of electromotive force (Laurie), (3) the specific volume curve.

The curve of fusion falls sharply from the melting point of gold to a eutectic point at 280° and 20 per cent. of tin. It then, after rising to a well-marked maximum point at 37.63 per cent. of tin and 418°, falls to a second eutectic point at 217° and 90 per cent. of tin, and finally it rises to the melting point of tin. On the section between the maximum point and the second eutectic point are two breaks, namely, at 308° and 60 per cent. of tin and at 252° and 80 per cent. of tin.

Three definite compounds exist, namely, AuSn, AuSn₂, and AuSn₄; the last two are formed without change of volume, the first with slight dilatation. AuSn forms a metallic silver-grey mass which is distinguished from gold and tin by its brittleness and hardness, and by the fact that its electrical conductivity is greater than that of all gold-tin alloys except those with 95 to 100 per cent. of gold; it is as resistant as pure gold to the action of acids. AuSn₂ is distinguished from the preceding by the form and size of its crystals. It undergoes transformation at 308° according to the equation $\text{AuSn}_2 \rightleftharpoons 0.597 \text{ AuSn} + \text{fused alloy (0.403 Au + 1.403 Sn)}$.

AuSn₄ is coloured gold-brown by the action of nitric acid, while AuSn₂ is unchanged. At 252°, AuSn₄ undergoes transformation according to the equation $\text{AuSn}_4 \rightleftharpoons 0.85 \text{ AuSn}_2 + \text{fused alloy (0.15 Au + 3.15 Sn)}$. D. H. J.

Potassium Iridochloronitrite. L. QUENNESSEN (*Compt. rend.*, 1905, 141, 258—259. Compare Leidié and Miolati and Gialdini, *Abstr.*, 1903, ii, 24).—When potassium iridium nitrite is treated with warm dilute hydrochloric acid, the liquid evaporated to dryness, and the residue dissolved in a saturated solution of potassium chloride, a

salt is precipitated, which, on recrystallisation from a boiling solution of potassium chloride, separates in small, yellow crystals, showing a blue tint when examined between crossed Nicols (compare Vezes, Abstr., 1893, ii, 213), and having the composition represented by the formula $K_{12}Ir_3Cl_{16}(NO_2)_8 \cdot 4H_2O$. The precipitation of this salt under these conditions illustrates the necessity, in using the nitrite method of separating metals of the platinum group, of completely destroying the nitro-compounds formed in cases where their presence is likely to interfere with the normal course of reactions.

T. A. H.

Mineralogical Chemistry.

Formation of Oceanic Salt Deposits. XLIII. Calcium Content of the Constant Solutions at 25°. JACOBUS H. VAN'T HOFF and WALTER C. BLASDALE (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 712—714).—This paper concludes the investigation in so far as calcium compounds at 25° are concerned, and the composition of all constant solutions, when saturated with the particular calcium salt with which the solutions are in equilibrium, is tabulated. For the sake of simplicity, gypsum, glauberite, and syngenite are the only salts taken into consideration, but the quantities of calcium found in the solutions cannot, however, on this account differ appreciably from the true equilibrium values.

Saturation with reference to NaCl and	Mols. per 1000 mols. H ₂ O.					
	Na ₂ Cl ₂ .	K ₂ Cl ₂ .	MgCl ₂ .	MgSO ₄ .	Na ₂ SO ₄ .	CaSO ₄ .
MgCl ₂ , 6H ₂ O	55.5	—	—	—	—	0.86
Na ₂ SO ₄	1.0	—	106.0	—	—	0.39
KCl	44.5	19.5	—	—	—	0.94
Na ₂ SO ₄	51.0	—	—	—	12.5	0.05
MgCl ₂ , 6H ₂ O, carnallite	1.0	0.5	105.0	—	—	0.38
KCl, carnallite	2.0	5.5	70.5	—	—	0.26
KCl, glaserite	44.0	20.0	—	—	4.5	0.03
Na ₂ SO ₄ , glaserite	44.0	10.5	—	—	14.5	0.02
Na ₂ SO ₄ , blödite	46.0	—	—	16.5	3.0	0.04
MgSO ₄ , 7H ₂ O, blödite	26.0	—	7.0	34.0	—	0.00
MgSO ₄ , 7H ₂ O, MgSO ₄ , 6H ₂ O	4.0	—	67.5	12.0	—	0.19
MgSO ₄ , 6H ₂ O, kieserite	2.5	—	79.0	9.5	—	0.12
Kieserite, MgCl ₂ , 6H ₂ O	1.0	—	101.0	5.0	—	0.25
KCl, glaserite, picromerite	23.0	14.0	21.5	14.0	—	0.08
KCl, picromerite, leonite	19.5	14.5	25.5	14.5	—	0.09
KCl, leonite, kainite	9.5	9.5	47.0	14.5	—	0.13
KCl, carnallite	2.5	6.0	68.0	5.0	—	0.24
Carnallite, kainite, kieserite	1.0	1.0	85.5	8.0	—	0.13
Na ₂ SO ₄ , glaserite, blödite	42.0	8.0	—	16.0	6.0	0.06
Glaserite, blödite, picromerite	27.5	10.5	16.5	18.5	—	0.08
Leonite, blödite, picromerite	22.0	10.5	23.0	19.0	—	0.08
Leonite, blödite, MgSO ₄ , 7H ₂ O	10.5	7.5	42.0	19.0	—	0.1
Leonite, kainite, MgSO ₄ , 7H ₂ O	9.0	7.5	45.0	19.5	—	0.09
MgSO ₄ , 6H ₂ O, kainite, MgSO ₄ , 7H ₂ O	3.5	4.0	66.5	13.0	—	0.2
MgSO ₄ , 6H ₂ O, kainite, kieserite	1.5	2.0	77.0	10.0	—	0.21
Carnallite, MgCl ₂ , 6H ₂ O, kieserite ...	1.0	0.5	100.0	5.0	—	0.15

H. M. D.

Chemistry of Ore Deposition. Precipitation of Copper by Natural Silicates. EUGENE C. SULLIVAN (*J. Amer. Chem. Soc.*, 1905, 27, 976—979).—A study has been made of the action of various natural silicates, including kaolin, shale, and feldspars, in a powdered state on solutions of copper sulphate. It is found that a double decomposition takes place, the copper being precipitated and an equivalent quantity of other bases (chiefly alkalis and alkaline earths) entering the solution. A certain amount of sulphate is precipitated with the copper, and it is at present uncertain whether this is due to adsorption of copper sulphate or to the precipitation of a basic copper salt. The quantity of copper precipitated varies with the fineness of the powdered silicate, and it appears therefore that the action takes place only on the surface of the particles. A specimen of shale in one case removed 95 per cent. and in another case the whole of the copper from a solution, the liquid being still neutral at the close of the experiment.

E. G.

Physiological Chemistry.

Preparation and Properties of Protoplasmic Extracts of Blood Corpuscles. AUGUSTE LUMIERE, LOUIS LUMIERE, and J. CHEVROTIER (*Compt. rend.*, 1905, 141, 142—143).—The substance is prepared by vigorously centrifugalising a mixture of blood and an isotonic liquid (1:20), collecting the globules, and washing several times with the same liquid. The whole mass is then diluted with distilled water to the original volume of the blood and subjected to alternate freezing and warming to 35° in order to break the envelopes of the cells. The mixture is again centrifugalised, the liquid decanted and rendered isotonic by adding sodium chloride. It is then filtered and kept in sterilised flasks.

The resulting liquid (hæmoplas) rapidly loses oxygen in a vacuum, acquiring a violet-black colour; the red colour is restored by agitation in air. It possesses the properties of an oxydase in a marked degree. It is very slightly toxic.

N. H. J. M.

Distribution of Saccharine Matters in the Plasma and in the Blood Corpuscles. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1905, 141, 175—177).—The determination of the saccharine matters in blood is far from giving the amount contained in the plasma, and the amount of these substances in corpuscles is not by any means negligible, being about a third of that contained in the plasma. When the amount of sugar in the blood increases suddenly, the corpuscles may contain as much as the plasma; or even more in exceptional cases of acute alcoholic intoxication.

N. H. J. M.

Digestion of Proteids in the Stomach. LUDWIG TOBLER (*Zeit. physiol. Chem.*, 1905, 45, 185—215).—The process of digestion of foods

in the dog's stomach has been examined with the aid of a duodenal fistula by a method details of which are given.

The digestion does not take place throughout the whole contents simultaneously, but solution takes place along the surface layers of the wall of the stomach, and a few minutes after a meal the expulsion of the first products of digestion begins, and these reach the intestine mainly in the form of thin liquids. With raw meat, some 50—65 per cent. enters the intestine in the dissolved form and only some 20 per cent. in the undissolved state. The dissolved proteids consist of peptones (80 per cent.) and albumoses (20—30 per cent.). In the stomach itself, considerable absorption of proteids occurs. When the pylorus reflex is retarded, the process is quicker and less complete, and then the amount of undissolved proteid increases, the absorption diminishes, and in the dissolved proteids the albumoses are in excess of the peptones.

J. J. S.

Secretion of the Human Pancreas. ALEXANDER ELLINGER and MAX COHN (*Zeit. physiol. Chem.*, 1905, 45, 28—37. Compare A. A. Walter, *Abstr.*, 1900, ii, 553; O. Schumm, *ibid.*, 1903, ii, 32, 439; Glaessner, *ibid.*, 1904, ii, 270).—The secretion from a human pancreatic fistula after an operation for cyst has been examined. The proportions of water, dry residue, nitrogen, coagulable proteids, globulins, albumins, and the specific gravity agree fairly closely with previous analyses by Schumm and by Glaessner. With regard to ferments, the secretion was far less active than Glaessner's normal pancreatic juice, but from a qualitative point of view was very similar. A few experiments have been made in order to determine the effect of different foods on the secretion. It appears that starchy foods diminish the amount of secretion to a considerable extent, and that the greatest secretion is obtained on a mixed diet.

J. J. S.

Pancreatic Juice rendered Active under the Combined Influence of Colloids and Electrolytes. LARGUIER DES BANCELS (*Compt. rend.*, 1905, 141, 144—145).—Inactive pancreatic juice is enabled to digest albumin impregnated with a suitable colloid, such as aniline-blue, methyl-violet, or Magdala-red, when electrolytes, such as the nitrates or sulphates of ammonium, calcium, or magnesium, are added.

N. H. J. M.

Maltase of Pancreatic Juice. H. BIERRY and E. F. TERROINE (*Compt. rend.*, 1905, 141, 146—147).—Whilst relatively large amounts of normal pancreatic juice are unable to hydrolyse maltose in twenty hours, hydrolysis takes place rapidly in presence of small amounts slightly acidified with acetic acid. Under similar conditions, starch is quickly converted into dextrose.

N. H. J. M.

Conjugated Glycuronic Acids in Bile. MANFRED BIAL (*Zeit. physiol. Chem.*, 1905, 45, 258—264).—Subcutaneous injections of menthol were made on a dog with gall fistula, and the presence of thymolglycuronic acid in the bile has been proved. The conjugated acid was precipitated from the bile as its insoluble lead salt, and after

boiling with dilute sulphuric acid gave a distinct odour of thymol and the characteristic bromophenylhydrazone of glycuronic acid. The conjugated acid is decomposed in contact with water and human faeces.

J. J. S.

The Substance which renders Active the Philocatalase in Animal Tissues. FR. BATTELLI and Mlle. L. STERN (*Compt. rend.*, 1905, 141, 139—142).—Aqueous extracts of animal tissues, heated to boiling and filtered, contain a substance which almost completely protects catalase from the action of anticatalase.

The different tissues of rabbits examined (liver, pancreas, kidney, blood, and muscles) do not differ materially as regards the amount of the substance; it is almost absent from the spleen, from which anti-catalase is prepared.

N. H. J. M.

Occurrence of Guanase in the Spleen of Oxen and its Non-occurrence in the Spleen of Pigs. WALTER JONES (*Zeit. physiol. Chem.*, 1905, 45, 84—91. Compare Abstr., 1904, ii, 625; Jones and Partridge, *ibid.*, i, 838; Schittenhelm, following abstract).—Further experiments show that adenine is completely transformed into hypoxanthine by extract of the spleen from pigs, whilst guanine contained in the same vessel and under exactly the same conditions remains unaltered. With extract of spleen from oxen, both guanine and adenine are decomposed, and only xanthine and uric acid are formed. The conclusion that the transformations of adenine into hypoxanthine and of guanine into xanthine are produced by two distinct enzymes, *adenase* and *guanase*, is thus confirmed. The transformation of hypoxanthine into xanthine and uric acid is attributed to an oxydase.

J. J. S.

Formation and Decomposition of Uric Acid in Extracts of the Organs of Oxen. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1905, 45, 121—151. Compare Abstr., 1904, ii, 752).—Extracts of the spleen, lungs, liver, intestine, muscle, and kidneys of oxen are capable of transforming purine bases into uric acid, and the extracts of kidneys, muscle, and liver can decompose this newly formed uric acid, whereas the spleen and lung extracts cannot do so.

In the case of guanine, this is first transformed into xanthine, and this into uric acid by a xanthine oxydase. With adenine, the stages are probably adenine \rightarrow hypoxanthine \rightarrow xanthine \rightarrow uric acid, and the yield of uric acid is almost quantitative when a good supply of oxygen is used. Thymus extracts can also transform amino- into hydroxy-purines. Since the formation and decomposition of uric acid do not proceed simultaneously in all organs, the two processes must be due to distinct ferments. This conclusion is confirmed by the fact that the ferments may be isolated by distinct methods. The ferment which induces the decomposition of uric acid is termed *uricolase*, or *uricolytic ferment*. Among its final decomposition products are glycine and carbamide.

The different results obtained when whole organs, for instance, pancreas, are left to autolysis may be accounted for by differences in the conditions, such as the presence of acid substances.

J. J. S.

Non-occurrence in the Spleen and Liver of Oxen of a Ferment which transforms Guanine into Xanthine. Reply to Jones, Partridge, and Winternitz. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1905, 45, 152—160. Compare Abstr., 1904, ii, 752; Jones and Partridge, *ibid.*, 1904, i, 838; Jones and Winternitz, this vol., ii, 333; Jones, preceding page).—Further experiments confirm the previous statement, that guanine in presence of oxygen is transformed into uric acid by extracts of the spleen of oxen, and the spleen must therefore contain the same ferment as is present in liver, muscles, &c.

The same results are obtained whether solutions of guanine hydrochloride or of guanine in dilute sodium hydroxide are used. The author considers it unnecessary to assume the presence of two distinct ferments, guanase and adenase, in these organs. [Jones's negative results were obtained with spleen of pigs.] J. J. S.

The Uricolytic Ferment. ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1905, 45, 161—165. Compare Wiener, Abstr., 1900, ii, 153; Burian, this vol., ii, 271; Ascoli, *Pflüger's Archiv*, 1898, 72, 340; Schittenhelm, Abstr., 1904, ii, 752, and preceding abstracts).—A good active solution of the uricolytic ferment can be obtained by Rosell's method of precipitation with uranyl acetate. The active properties of the ferment are destroyed by heating at 80—100°. J. J. S.

Fate of Vanillin in the Animal Body. Y. KOTAKE (*Zeit. physiol. Chem.*, 1905, 45, 320—325. Compare Preusse, *ibid.*, 1880, 4, 213).—Vanillin is oxidised to vanillic acid, which combines with glycuronic acid to form *glycurovanillic acid*, the barium salt of which, $C_{14}H_{16}O_{11}Ba$, has been analysed. The salt has $[\alpha]_D - 37.94^\circ$. The acid is precipitated from its solutions by basic lead acetate, does not reduce alkaline solutions of cupric salts, and is hydrolysed when boiled with dilute acids. J. J. S.

Amounts and Origin of Purine Bases in Human Fæces. II. MARTIN KRÜGER and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1905, 45, 14—27. Compare Abstr., 1902, ii, 412).—The fæces are digested with dilute sulphuric acid, neutralised with sodium hydroxide to avoid the large amount of washing necessary when barium hydroxide is used, filtered, and the purine derivatives precipitated by the copper method. This gives too high results, as certain albumins and albuminoses are also precipitated. Good results may be obtained by treating the first copper precipitate with sodium sulphide, boiling the filtrate, and reprecipitating the purine bases by the copper or by the silver method.

The amount of nitrogen in the form of purine bases is not less than 0.186 gram per diem. The purine bases are regarded as mainly derived from the secretive organs, namely, liver, spleen, and pancreas, and also to a certain extent from the epithelium of the intestine.

J. J. S.

Chemistry of Vegetable Physiology and Agriculture.

Malt Oxydase. WLADIMIR ISSAJEW (*Zeit. physiol. Chem.*, 1905, 45, 331—350. Compare Abstr., 1904, i, 959).—Extracts of barley, malt, or diastase with water, alcohol, or aqueous glycerol contain an oxydase. The extractions are best made with 50 per cent. glycerol, as sterilisation by means of bacteria filters is then unnecessary. The ferment present can oxidise the small amounts of oxidisable substances present in the solution, and also various organic compounds which are added. It is highly probable that three distinct ferments are present, an oxydase, a peroxydase, and a catalase. The oxydase is not readily destroyed by heating the solution in boiling water, but its action is reduced; addition of acids and alkalis produces the same effect. The following compounds are all oxidised: *p*-aminophenol, the di- and trihydroxybenzenes, gallic acid, and potassium gallate. *p*-Aminophenol is oxidised much more readily than quinol, ortho-compounds appear to be oxidised more readily than the corresponding para-, and these more readily than meta-compounds. Potassium gallate is decomposed the most readily. Numerous other compounds (phenols, phenol ethers, sugars, &c.) were examined, but were not oxidised to any appreciable extent.

Malt oxydase is only partially absorbed by animal charcoal at the ordinary temperature. Mercuric chloride or tannin destroys the activity of the oxydase, whereas small amounts of alcohol increase it. Dilute manganous sulphate solutions have no action, and concentrated solutions have a retarding effect.

It appears that the activity of the oxydase in barley increases during the process of malting up to the eighth day, then remains constant, but falls on air-drying, and still further on drying at a high temperature.
J. J. S.

Assimilation of Free, Elementary Nitrogen by Micro-organisms. J. VOGEL (*Centr. Bakt. Par.*, 1905, 15, ii, 33—53).—A *résumé* of recent investigations on the subject.
N. H. J. M.

Bacillus Macerans, a Bacillus which produces Acetone. FRANZ SCHARDINGER (*Centr. Bakt. Par.*, 1905, 14, ii, 772—781).—The bacillus was first noticed in a nutritive mixture, the chief constituent of which was potato pulp, and was subsequently found in the mud from flax pits. Its chief characteristics are a very considerable power of breaking down vegetable cells, and of fermenting carbohydrates with production of acetone, acetic acid, and formic acid. Lactic and succinic acids are not produced.

Bacillus macerans may be appropriately placed in the group of the hay-*Bacilli*. In the great power of the spores in resisting high temperatures, it closely resembles the hay-potato bacillus.

N. H. J. M.

Decomposition of Fats. OTTO RAHN (*Centr. Bakt. Par.*, 1905, 15, ii, 53—61).—Only few bacteria are known which decompose fats; the property is more common in the case of mould-fungi. Fatty acids are equally consumed by bacteria, whilst moulds more readily attack the lower fatty acids. The oxidation of acids seems always to be complete without formation of secondary products.
N. H. J. M.

Formation of Hydrogen Sulphide by Yeast. RICHARD SCHANDER (*Bied. Centr.*, 1905, 34, 553—556; from *Jahresber. Verein. Vertreter angew. Bot.*, 1903—1904, 85—121).—Yeasts produce hydrogen sulphide from free sulphur and sulphur compounds; sulphates are more readily decomposed than organic sulphur compounds. In addition to hydrogen sulphide, organic compounds containing sulphur (probably mercaptols) are produced.

The activity of yeasts is stimulated by sulphates, and especially by free sulphur.
N. H. J. M.

The Acidity of Milk. C. J. KONING (*Milchw. Zentr.*, 1905, 1, 289—305; 337—356).—No relation exists between the acidity and the total number of bacteria contained in a sample of ordinary milk, and the loss of carbon dioxide is not balanced by the production of lactic acid. Only when the acidity exceeds a certain limit does the acidity during a certain phase correspondingly increase with the number of bacteria growing in that phase. The relation is also observed when sterilised milk is inoculated with lactic acid bacteria. The age of a sample of milk cannot be arrived at from an estimation of the rise in acidity when the milk is kept at a fixed temperature for a certain number of hours, the so-called age of milk depending on the development of the bacterial flora, and being but little influenced by time.
W. P. S.

Sterilisation of Milk with Hydrogen Peroxide, with Special Reference to Budde's Process. MISTISLAW LUKIN (*Centr. Bakt. Par.*, 1905, 15, ii, 20—32).—The action of hydrogen peroxide diminishes as the acidity increases; it is greater at 37° than at the ordinary temperature. Sterilisation of milk merely by addition of hydrogen peroxide is not practicable. The ordinary 3 per cent. preparation would have to be used in quantities which involve considerable dilution of the milk.

In Budde's method, the warming of the milk to 52° enables the quantity of hydrogen peroxide to be reduced considerably, the amounts required being 0·03 to 0·05, according to the amount of bacteria present.

Experiments with inoculated milk showed that the hay-bacillus, *Streptococcus pyogenes*, and *Bacillus coli commune* are all destroyed by Budde's method.

Different substances have been suggested for removing the hydrogen peroxide from the sterilised milk, but further experiments are necessary.
N. H. J. M.

Development of Green Plants in Light, in Absence of Carbon Dioxide, in an Artificial Soil containing Amides. JULES LEFÈVRE (*Compt. rend.*, 1905, 141, 211—213).—Plants grew normally without carbon dioxide in ignited sand, containing, in addition to Detmer's mineral food, a mixture of tyrosine (0.1), glycine (0.4), alanine (0.4), oxamide (0.1), and leucine (0.1 gram to 350 grams of sand). No carbon dioxide was liberated from the organic matter present.
N. H. J. M.

Chemical Composition of the Cell Membrane in various Cryptogams. KARL MÜLLER (*Zeit. physiol. Chem.*, 1905, 45, 265—298. Compare Schulze, *Abstr.*, 1890, 283; 1892, 907; 1894, ii, 250; Gilson, *ibid.*, 1895, i, 323; ii, 323, 408; Winterstein, 1896, ii, 210).—The following have been examined: Algæ—*Cladophora glomerata*. Lichens—*Cladonia rangiferina*, *Cetraria islandica*, *Evernia prunastri*, *Ramalina fraxinea*. Liverworts—*Leioscyphus (Jungermannia) Tylori*, *Mastigobryum trilobatum*. Mosses—*Sphagnum cuspidatum*, *Polytrichum commune*. The nature of the cell membrane was determined by an examination of the products of hydrolysis. The chief constituents are celluloses, either dextrose-cellulose or mannose-cellulose, and hemicelluloses, such as xylan, galactan, dextran, araban, methylpentosan. Chitin is present in small quantities in *Cladonia* and *Evernia*. Everniin (compare Stüde, *Annalen*, 131, 241) has the composition $C_7H_{15}O_6$.
J. J. S.

Nature of the Cyanogenetic Glucoside of the Elder. L. GUIGNARD and JULES HOUDAS (*Compt. rend.*, 1905, 141, 236—238. Compare this vol., ii, 604, and Bourquelot and Danjou, *ibid.*, ii, 605).—The authors conclude that the cyanogenetic glucoside contained in the leaves of the elder (*Sambucus nigra*) is amygdalin, since the aqueous liquid obtained by macerating the comminuted leaves in water and distilling in a current of steam contains benzaldehyde, identified by means of its semicarbazone.
T. A. H.

Coffee Seeds without Caffeine. GABRIEL BERTRAND (*Compt. rend.*, 1905, 141, 209—211).—The seeds of different species of coffee contain 1 to 1.5 per cent. of caffeine. *Coffea Humblotiana*, which is very similar to *C. arabica*, does not contain, however, any trace of caffeine, and this is also true of three new species, *C. Gullenii*, *C. Bonnierii*, and *C. Mogenetii*.

The absence of caffeine is not due to conditions of soil or climate, since *Coffea arabica* grown under the same conditions was found to contain 1.34 per cent.
N. H. J. M.

Quantitative Investigation of the Distribution of the Alkaloids in the Organs of Datura Stramonium. JULIUS FELDHAUS (*Arch. Pharm.*, 1905, 243, 328—348).—This paper is of interest chiefly from the standpoint of physiological botany. The percentage of alkaloid in the dried material varied from 1.39 in the ribs of the leaves to 0.082 in the ripe pericarps, 0.9 in the main stem, and

0.10 in the main root; in most parts the percentage lay between 0.3 and 0.6.

In the case of the seeds, the percentage varied from 0.21 to 0.48, according to the locality (in Germany and Switzerland) from which the drug was procured; it varies also with the year, having been 0.33, 0.48, and 0.34 in the case of seed harvested at Marburg in the years 1900, 1901, and 1902 respectively. C. F. B.

Weathered Hay. WALTER F. SUTHERST (*Chem. News*, 1905, 92, 61).—Hay exposed to rain loses carbohydrates, amino-compounds, and ash constituents. D. A. L.

Pond Feeding Experiments at Hellendorf and Geeste in 1903. W. CRONHEIM and E. GIESECKE (*Bied. Centr.*, 1905, 34, 543—546; from *Fisch. Zeit.*, 1904, 7, No. 42).—The foods employed were crushed maize, barley, blue lupins, or fish meal, and it was found advantageous to continue feeding in September when the weather continues to be warm. The amount of food consumed was 3.956 kilograms per kilogram of fish. Application of manure is desirable.

As regards mineral food, calcium and phosphoric acid are sufficiently abundant under ordinary conditions; it may, however, be desirable to supply potassium either in the food or as manure. N. H. J. M.

New Apparatus for Determining the Ammonia-absorption Power of Soils. FERDINAND WOHLTMANN and PH. SCHNEIDER (*Chem. Zeit.*, 1905, 29, 810—811).—The dry material is brought into contact with dry ammonia, and the absorption is measured by the rising of the mercury in the graduated tube. For a description of the apparatus, the original paper and illustration must be consulted.

L. DE K.

Influence of Fat and other Substances on Milk Production when given in Addition to a Scanty Basal Food. AUGUST MORGEN, CARL BEGER, and GUSTAV FINGERLING (*Landw. Versuchs-stat.*, 1905, 62, 251—386).—Addition of fat (earth-nut oil) in suitable quantity is especially suitable for the production of milk-fat, and probably no other kind of food has a similar effect. Proteids are favourable to milk production, but have no specific action on the production of milk-fat. Carbohydrates have no effect on the yield or on the production of milk-fat.

The refractometer number of the fat of milk is raised by addition of fat to the food.

The three kinds of food (fat, proteids, and carbohydrates) do not show any marked differences as regards effect on live weight.

Addition of moderate amounts of fat to a normal food considerably increases the yield of milk, and also increases the percentage of fat in the milk by 0.14 per cent. Larger amounts of fat give a considerable further increase in the amount of milk, but vary in their action on the production of fat, being sometimes favourable and sometimes unfavourable. N. H. J. M.

"Basic Slag-ammonia," a New Manure ; its Composition and Results of Manurial Experiments in 1904. MÜLLER (*Bied. Centr.*, 1905, **34**, 513—514 ; from *Illust. landw. Zeit.*, 1905, **25**, 303).—The manure is prepared from basic slag or superphosphates and ammonium salts. The results of experiments with wheat, oats, potatoes, mangolds, and rye, in which the manure (from basic slag) was compared with sodium nitrate, basic slag, and potassium salts, were very satisfactory. The manure should not be ploughed in deep, but applied as a top dressing.

If soon used, the manure loses very little nitrogen. N. H. J. M.

Manurial Experiments at the Agricultural Experiment Station, Marburg. E. HASELHOFF (*Bied. Centr.*, 1905, **34**, 515—518 ; from *Jahresber. landw. Versuchs-stat. Marburg*, 1904—5).—Experiments with calcium cyanamide showed that germination is affected by the presence of 0.025 gram per 100 grams of soil. Injury is, however, avoided if the calcium cyanamide is applied some time before sowing the seed. In field experiments, the manure gives good results. "Basic slag-ammonia" gives good results both as a phosphatic and a nitrogenous manure, but its employment is not recommended owing to the loss of nitrogen which it must undergo (compare preceding abstract). N. H. J. M.

Manurial Value of Molasses as compared with Ammonium Sulphate and 40 per cent. Potassium Salts. LILIENTHAL (*Bied. Centr.*, 1905, **34**, 514—515 ; from *Illust. landw. Zeit.*, 1905, **25**, 319).—The dried molasses contain $N=3.5$ and $K_2O=13$ per cent., but no phosphoric acid. As compared with ammonium salts and 40 per cent. potassium salts, the manure gives favourable results with respect to the quality of potatoes ; the yield of potatoes is about the same in both cases. N. H. J. M.

Function of the Sodium when used in Sodium Nitrate. HOMER J. WHEELER, BURT L. HARTWELL, and G. E. ADAMS (16th *Ann. Rep. Rhode Island Agr. Exper. Stat.*, 1902—3, 237—267).—Plant growth is greatly influenced by the chemical reaction of the soil, or by compounds formed as a result of the reaction. Sodium nitrate leaves a basic residue owing to the nitrogen being appropriated by the plant, whilst for the same reason ammonium sulphate leaves an acid residue. Differences in yields produced by ammonium sulphate and sodium nitrate are attributed chiefly to this difference in chemical reaction produced in the soil. N. H. J. M.

Analytical Chemistry.

Simplified Elementary Analysis and its Technical Application. MAXIMILIANO DENNSTEDT (*Zeit. angew. Chem.*, 1905, 18, 1134—1137. Compare Abstr., 1903, ii, 103; this vol., ii, 202).—The author demonstrates the applicability of his method of elementary analysis to various technical products such as coal, mineral oils, and pyrites.

Heraeus' electric combustion furnace may also be modified as described in the paper. A. McK.

Apparatus for Generation of Hydrogen Sulphide, &c. HEINRICH BILTZ (*Chem. Zeit.*, 1905, 29, 809).—A Clement-Winkler's apparatus of larger size and made of stoneware. Any suitable acid may be used. L. DE K.

Titrimetric Estimation of Chlorates and Bromates. MAX SCHOLTZ (*Arch. Pharm.*, 1905, 243, 353—358).—Of the chlorate 0.2—0.3 gram, or of the bromate 0.3—0.4 gram, is dissolved in about 100 c.c. of water, 10 c.c. of nitric acid of sp. gr. 1.2 and 10 c.c. of a 10 per cent. solution of sodium nitrite are added, and the whole is allowed to remain at the ordinary temperature for ten to fifteen minutes in the case of the chlorate, for five minutes in the case of the bromate. Then a measured excess, say 30 c.c., of *N*/10 silver nitrate solution is added and 5 c.c. of a saturated solution of iron alum, and the excess of silver is titrated with *N*/10 ammonium thiocyanate solution. Of the *N*/10 silver solution, 1 c.c. = 0.012245 gram of potassium chlorate or 0.0167 gram of potassium bromate. The nitrous acid reduces the chloric or bromic acid formed to hydrochloric or hydrobromic acid. Iodic acid is not reduced by nitrous acid.

C. F. B.

Assay of Concentrated Nitric Acids by the Specific Gravity. GEORG LUNGE (*Chem. Zeit.*, 1905, 29, 933—934).—A detailed reply to Winteler (this vol., ii, 553). The sp. gr. tables constructed by the author and Rey (Abstr., 1892, 11, 13) give perfectly correct results, and their accuracy has since been confirmed by Veley and Manley (*Trans.*, 1903, 85, 1015) and others. Hyponitric acid should, of course, be allowed for. L. DE K.

Electrolytic Estimation of Small Quantities of Arsenic. HEINRICH FRERICHs and G. RODENBERG (*Arch. Pharm.*, 1905, 243, 348—353).—The mixture of hydrogen with hydrogen arsenide is generated in an apparatus similar to that of Trotman (Abstr., 1904, ii, 291), except that the perishable parchment diaphragm is replaced by a

porous cup, cut from the end of a clay battery cell, into which is cemented a glass tube which surrounds the cathode and is fitted above with an india-rubber stopper pierced by a delivery tube, &c. The issuing gas passes first through a small tube containing pumice moistened with lead acetate, and then into an absorption tube containing ammoniacal standard silver nitrate solution; this solution is finally acidified with nitric acid, and the excess of silver is titrated with thiocyanate. The absorption tube has the form of a U-tube with a large bulb at the bottom of each limb, these being connected by a narrow tube rising slightly, on which 5 or 6 small bulbs are blown. This part of the apparatus, as well as the method, has been employed by Mai and Hurt; but whereas with their cell electrolysis for three hours is necessary when 0.02 gram of arsenious oxide is present, half an hour suffices with the cell just described. In the case of arsenic acid, it is better first to reduce this with sulphurous acid to the arsenious state; otherwise electrolysis for at least three hours is necessary. A current of 2—3 amperes at a pressure of 16 volts was employed.

C. F. B.

Estimation of Arsenic as Magnesium Pyroarsenate. JUAN FAGES VIRGILI (*Zeit. anal. Chem.*, 1905, 44, 492—516).—The results obtained by this method are too low unless particular precautions are taken in igniting the precipitate of magnesium ammonium arsenate and the filter on which it has been collected. The solubility of the precipitate in the wash-water should also be taken into account. The author finds it better to dissolve the precipitate off the filter with nitric acid, evaporate the solution, and ignite the residue obtained. Each 100 c.c. of solution and ammoniacal wash-water dissolves an amount of ammonium magnesium arsenate corresponding with 0.0013 gram of arsenic (As), and this correction must be applied to the final results. If, however, not less than 250 c.c. or more than 350 c.c. of solution and wash-water be used for each 0.1 gram of arsenic, the correction may be neglected, as the impurities occluded by the precipitate compensate for the solubility.

W. P. S.

Occurrence of Boric Acid in Common Salt. RUDOLF HEFELMANN (*Zeit. öffentl. Chem.*, 1905, 11, 231—234).—Although the salt obtained from some Italian and Swiss mines undoubtedly contains boric acid, the quantity of the latter present is extremely small, varying from 0.0006 to 0.0030 per cent. The quantity of boric acid introduced into foods by the use of this salt is too minute to be detected by the usual tests.

W. P. S.

Separation of Metals by Volatilisation in a Current of Hydrochloric Acid Gas. CARL FRIEDHEIM and LUDWIG JACOBUS (*Zeit. anal. Chem.*, 1905, 44, 465—491).—Results are given of a number of separations of metals by this method, which was originally proposed by Jannasch (*Abstr.*, 1895, ii, 89, 462). The process consists in heating a mixture of the oxides or salts of the metals in a current of pure dry hydrogen chloride. The volatile chloride collected

in the receiver of the apparatus and the residue in the decomposition vessel are then separately estimated. The separations carried out by the authors were: arsenic from lead, arsenic from copper, arsenic from iron, tin from lead, tin from copper, tin from iron, bismuth from lead, bismuth from copper, and bismuth from cobalt and nickel. In almost all cases appreciable quantities of the volatile metal remain in the non-volatile residue. The best results are obtained in the separation of tin from copper, practically quantitative results being yielded.

W. P. S.

Detection and Estimation of Sodium in Presence of Lithium by means of Hydrofluosilicic Acid. C. REICHARD (*Chem. Zeit.*, 1905, 29, 861—862).—Not only potassium, but also sodium, may be quantitatively precipitated by means of hydrofluosilicic acid, whilst lithium is not at all affected. The respective precipitates are then ignited (the filter being burnt separately) and weighed as silicofluorides.

In case both potassium and sodium are present, the mixed precipitate is heated with a little hydrofluoric acid and sulphuric acid and finally weighed as mixed sulphate. After estimating the sulphur trioxide contained therein, the amount of the respective metals may be found by the usual calculation.

L. DE K.

Electrolytic Estimation of Zinc. K. JENE (*Chem. Zeit.*, 1905, 29, 803—804).—0.5 gram of zinc ore is dissolved in nitro-hydrochloric acid, the solution is evaporated to dryness, and the residue heated with 1—2 c.c. of dilute sulphuric acid (1:1) until fumes appear. When cold, the mass is taken up with boiling water and filtered. The filtrate and washings, which need not exceed 80—100 c.c., are placed in a weighed copper-coated platinum dish, 4—7 grams of sodium hydroxide having first been added. Neglecting any undissolved metallic hydroxides, the liquid is at once submitted to electrolysis at a temperature of 50°, using 1 ampere and a potential difference of 3.8—4.2 volts. The zinc is completely deposited within 1½—2 hours. Without interrupting the current, the dish is well rinsed, first with cold water and then with absolute alcohol. After drying for a few minutes in the air-bath, the dish is reweighed.

L. DE K.

Rapid Method for the Detection of Traces of Zinc in Worts, Beer, Wine, &c. J. BRAND (*Chem. Centr.*, 1905, ii, 515; from *Zeit. ges. Brauw.*, 28, 438—440).—Five hundred c.c. of the sample are slightly acidified with hydrochloric acid, and a few drops of potassium ferrocyanide are added. If no precipitate forms, zinc is absent, but if there is any precipitate this should be collected and incinerated on a platinum lid. The ash is then digested with acetic acid and tested for zinc with hydrogen sulphide.

L. DE K.

Titration of Ferrous Iron with Permanganate in Presence of Hydrochloric Acid. GREGORY P. BAXTER and HARRY LOUIS FREVERT (*Amer. Chem. J.*, 1905, 34, 109—116).—Baxter and Zanetti (this vol., ii, 490) have shown that oxalic acid may be accurately

titrated with permanganate in presence of free hydrochloric acid without addition of manganous sulphate, provided the temperature at the beginning of the titration is above 70° .

The authors prove by a series of experiments that ferrous iron cannot be accurately titrated with permanganate unless about one gram of manganous sulphate is added; the temperature may then be raised even to 95° .

Fairly accurate results may, however, be obtained without addition of manganous sulphate by titrating with permanganate at $80-90^{\circ}$ in presence of but little free hydrochloric acid, and afterwards applying a negative correction of 0.3 per cent.

L. DE K.

Estimation of Metallic Iron in Ferrum Redactum. A. CHRISTENSEN (*Zeit. anal. Chem.*, 1905, 44, 535—540).—An accurately weighed portion of about 0.5 gram of the sample is placed in a 100 c.c. flask which has previously been filled with carbon dioxide. Fifty c.c. of neutral ferric chloride solution, prepared by dissolving 1 part of anhydrous ferric chloride in 10 parts of water, are added, the flask is closed, and shaken for twenty minutes. The volume is then made up to 100 c.c. with boiled water, and the contents of the flask well mixed. After standing for twenty-four hours, 20 c.c. of the clear supernatant solution are withdrawn, transferred to a flask containing 50 c.c. of 10 per cent. sulphuric acid and filled with carbon dioxide, and titrated with $N/10$ potassium permanganate solution. The volume of the latter required corresponds with the quantity of ferrous chloride produced by the reaction, and the amount of metallic iron present is calculated from the equation $\text{Fe} + 2\text{FeCl}_3 = 3\text{FeCl}_2$.

W. P. S.

Gasometric Estimation of Metallic Iron in Ferrum Redactum. FERDINAND BARMWATER (*Zeit. anal. Chem.*, 1905, 44, 541—543).—About one gram of the sample is weighed out into a small test-tube and placed in an evolution flask of 400 c.c. capacity, provided with an india-rubber stopper through which pass two glass tubes. One of these tubes is connected with a U-shaped gas-measuring tube. The latter has two bulbs blown on the limb next the evolution flask and is graduated, the volume of gas which the limb will hold being about 500 c.c. The other limb is narrow and carries a side-tube which serves as a siphon for levelling the water with which the tube is filled. At the commencement of the estimation, the evolution flask is filled with hydrogen after first adding the necessary volume of 20 per cent. sulphuric acid. Both flask and measuring tube are surrounded by vessels containing water. The *ferrum redactum* in the test-tube is brought into contact with the acid in the flask and the evolved hydrogen collected in the measuring tube. The reaction is completed by heating the water surrounding the flask. When no more gas comes over, the flask is allowed to cool to the initial temperature, and the volume of the collected gas read off after bringing the level of the water in both limbs of the tube to the same height. From the volume of gas obtained, the amount of metallic iron in the sample may be calculated.

W. P. S.

Estimation of Antimony as Trisulphide and the Separation of Antimony from Tin. GEORG VORTMANN and A. METZL (*Zeit. anal. Chem.*, 1905, 44, 525—535).—Hydrochloric acid is added to the solution containing the antimony in the proportion of 24 c.c. of the concentrated acid to each 100 c.c. of the neutral solution. The mixture is then heated to boiling and treated with a current of hydrogen sulphide gas. The yellow sulphide, which is at first precipitated, gradually becomes red, then brown, and finally black and crystalline. An equal volume of water is now added and a little more hydrogen sulphide passed through the solution. The precipitate is collected on a tared filter, washed with water, then with alcohol, and dried. Small quantities of free sulphur contained in the precipitate may be removed by extraction with carbon disulphide. After again drying, the precipitate is weighed. An alternative method consists in placing the moist filter and precipitate in a crucible, and adding about three grams of a mixture of three parts of ferric oxide with one part of ferric nitrate. The crucible and its contents are then cautiously heated, the flame being increased to a blast at the end of the operation. The quantity of residue left by the iron mixture is found by a previous experiment and subtracted.

Antimony may be quantitatively separated from tin by dissolving the mixed sulphides in a little hydrochloric acid (1:1), neutralising the solution by the addition of sodium hydroxide, and diluting to a volume of 60 c.c. An equal volume (60 c.c.) of phosphoric acid of sp. gr. 1.3 and 24 c.c. of concentrated hydrochloric acid are then added and the solution treated at the boiling temperature with hydrogen sulphide. The black precipitated antimony trisulphide is collected and weighed as previously described. The filtrate containing the whole of the tin in solution is nearly neutralised, diluted with an equal volume of water, warmed, and the tin precipitated as the sulphide in the usual manner.

W. P. S.

Estimation of Ethyl and Methyl Alcohol in Mixtures by the Immersion Refractometer. ALBERT E. LEACH and HERMANN C. LYTCHGOE (*J. Amer. Chem. Soc.*, 1905, 27, 964—972).—Whilst the U.S.P. spirit containing 91 per cent. by weight of absolute ethyl alcohol gives a reading of 98.3° at 20° with the immersion refractometer, a 91 per cent. methyl alcohol only gives a reading of 14.9° .

In order to detect methyl alcohol in, for example, tinctures, these are subjected to distillation, and the joint ethyl and methyl alcohols are found from the sp. gr., as there is practically no difference in density between the two alcohols. If, now, the result obtained by the refractometer corresponds with that calculated from the sp. gr. (the authors use *Hegnner's tables*), the spirit is pure, but if decidedly lower, methyl alcohol is present and its amount may be calculated by referring to the tables in the original.

L. DE K.

Action of Aldehydes on Mercuric Oxide in Alkaline Solution. Distinction between Acetaldehyde and Formaldehyde. ALEXANDRE LEYS (*J. Pharm. Chim.*, 1905, [vi], 22, 107—112).—A solution of one gram of mercuric oxide dissolved by gentle warming in

100 c.c. of a freshly prepared 5 per cent. solution of sodium sulphite after filtering out of contact with ammoniacal vapours, forms a reagent for aldehydes containing the $-\text{CH}_2\cdot\text{CHO}$ group, and may therefore be used for distinguishing acetaldehyde from formaldehyde. The reagent, treated with a few drops of dilute acetaldehyde solution and an equal volume of very dilute sodium hydroxide, produces in the cold a heavy white precipitate, to which the formula $\text{Hg}\cdot\text{CH}\cdot\text{CH}\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}\text{Hg}$ is assigned; alcohol may be added if necessary to keep the aldehyde in solution. Terpenes are the only substances producing a similar precipitate under those circumstances. Acetone and acetylacetone also produce precipitates, but only on warming. P. H.

Indirect Estimation of Aldehydes in Oil of Lemon. ENRICO BERTÉ (*Chem. Zeit.*, 1905, 29, 805—806).—The percentage of aldehydes in oil of lemon may be calculated by means of the formula $C = \frac{100(A - a)}{A}$, in which a represents the polarisation of the sample, A the polarisation of the sample freed from aldehydes, and C the percentage of aldehydes.

The oil is deprived of aldehydes by heating 10 c.c. of the sample for fifteen minutes with 50 c.c. of a saturated solution of potassium hydrogen sulphite in a boiling water-bath with constant shaking. To prevent volatilisation, the flask is fitted with a cork, through which passes a tube 40—45 cm. long. Finally, the supernatant oil is decanted, washed with a little water, and then dried over a little anhydrous sodium sulphate. A large number of experiments are communicated.

L. DE K.

Polarimetric Determination of Sucrose. FRANCIS WATTS and HAROLD A. TEMPANY (*West Indian Bulletin*, 1905, 6, 52—60).—In reading sucrose solutions in the polarimeter at tropical temperatures, the authors recommend, when no clarifying reagent is necessary, the solution of 26 grams of the sugar in 100 true c.c. of water. The correction for the temperature change of the quartz is then made by Jobin's formula, and that for the change of the polarisation by the formula: polarisation $+ 0\cdot00023tN$, where t is the difference between the temperature of observation and that at which the instrument was standardised, and N is the Ventzke-Scheibler reading observed. Both corrections may be made by the formula: polarisation $+ 0\cdot00039tN$.

When clarification by means of lead acetate is necessary, a very considerable error is introduced if no account is taken of the volume occupied by the lead precipitate. A method which obviates this error, and which is yet much simpler than the actual direct or indirect measurement of the volume of the precipitate, has been given by Horne (*Abstr.*, 1904, ii, 451). It consists in making the solution up to 100 c.c. and then adding dry anhydrous basic lead acetate, excess of which should be avoided. This procedure leads to results approximating closely to the truth.

T. H. P.

Influence of Invert Sugar on the Estimation of Crystallisable Sugar with Reference to the Yield of Refined Sugar.

MAXIME CARIMANTRAND (*Bull. Soc. chim.*, 1905, [iii], 33, 795—799).—The author finds that, contrary to the opinion recently published, uncrystallisable sugar (invert sugar) diminishes the rotatory power of crystallisable sugar to which it is added, and that, consequently, Clerget's method is the one giving most exactly the proportions of the two sugars present. If tartaric acid is used for the inversion, the temperature and time have little influence on the inverted products, sugar syrups of 40° B. being quite colourless when completely inverted. Inversion with tartaric acid is the more rapid and complete the nearer the sp. gr. of the solution is to 35—36° B. With 10 per cent. sugar solutions, inversion is slow, and it does not take place at all with cane molasses containing a large proportion of invert sugar.

The proportion of uncrystallisable sugar in raw sugars is nearly always less than 5 per cent., so that inversion with tartaric or hydrochloric acid is unnecessary, since this amount does not appreciably influence the rotation of the sucrose. When, however, the proportion of invert sugar reaches 10 per cent. or more, the sugar should be first defecated with basic lead acetate and Clerget's method then employed.

T. H. P.

Detection of Wood-fibre. W. HERZBERG (*Chem. Centr.*, 1905, ii, 359—360; from *Mitt. K. Materialprüfungsamt*, 1904, 22, 293—294).

—The test for wood pulp in paper with phloroglucinol is somewhat interfered with by the presence of colouring matter, such as metanil-yellow. Spots caused by metanil-yellow are, however, of a more uniform colour than those caused by wood-fibre; they also fade much more quickly and show a violet zone. In case of doubt, the paper is moistened with hydrochloric acid; and if this gives no colour the reaction with phloroglucinol is due to wood-fibre. If the acid should give a red spot, recourse should be had to a microscopical examination.

L. DE K.

Saponification of Beeswax. F. SCHWARTZ (*Zeit. öffentl. Chem.*, 1905, 11, 301—302).—A reply to Cohn (*ibid.*, 58). The author again states that one hour's boiling with an $N/2$ solution of potassium hydroxide in absolute alcohol is sufficient for the complete saponification of the wax. It is also recommended to add more alcohol before titrating the excess of alkali with $N/2$ hydrochloric acid so as to prevent a dissociation of the soap by the water introduced.

L. DE K.

Rosin Spirit, Pine Wood Oils, and Turpentine. EDUARD VALENTA (*Chem. Zeit.*, 1905, 29, 807—808).—Rosin spirit (pinolin) may be detected in commercial turpentine by collecting the fraction distilling below 160° and applying the following reaction. One part of the distillate is mixed with 1—2 parts of a 6 per cent. solution of iodine in chloroform or carbon tetrachloride, when in the presence of pinolin a green or olive-green coloration is obtained on warming. The same green colour is obtained on adding acetic anhydride and a drop of

sulphuric acid. Pine wood oils, which are really only turpentine contaminated with empyreumatic products, may be identified by their reducing action on a solution of gold chloride. If 5 c.c. of a 10 per cent. solution of potassium iodide is shaken with 10 c.c. of fresh turpentine and 10 c.c. of carbon disulphide, a yellow potassium iodide layer and a rose-coloured oily layer are obtained. Pine wood oils yield a yellowish-red oily layer. Rosin spirit, petroleum, and rosin oil give more or less pale-yellow oily layers. In the case of pine wood oils the oily layer also becomes turbid.

For further reactions, the tables in the original paper should be consulted.

L. DE K.

Detection of Salicylic Acid in Foods. FELICE GORNI (*Chem. Centr.*, 1905, ii, 519; from *Boll. Chim. Farm.*, 44, 409—414).—The presence of lactic and other organic acids interferes with the ferric chloride test for salicylic acid. In order fully to ensure the absence of these acids, it is recommended to extract the salicylic acid not with pure ether, but with a mixture of equal volumes of ether and light petroleum.

L. DE K.

Estimation of Glycuronic Acid. CARL NEUBERG (*Zeit. physiol. Chem.*, 1905, 45, 183—184).—Polemical (compare Tollens, this vol., ii, 559).

J. J. S.

The True Dropping Point and an Apparatus for Determining it. LEO UBBELOHDE (*Zeit. angew. Chem.*, 1905, 18, 1220—1225).—Objection is raised to Pohl's and to Finkener's methods for determining the dropping point of fats, &c. The true dropping point is defined as the temperature at which a single drop separates under the influence of its own weight from a mass of the substance which has been uniformly heated, and the amount and weight of which do not influence the drop.

An apparatus for determining the true dropping point is described.

A. McK.

Detection and Estimation of Antipyrine in Pyramidone. GUSTAVE PATEIN (*J. Pharm. Chim.*, 1905, [vi], 22, 5—8).—A test originally proposed by Bourcet may be used for the detection of antipyrine. 0.2 gram of the sample is dissolved in 5 c.c. of water and treated with two drops of sulphuric acid and a few crystals of sodium nitrite. In the case of pure pyramidone, an intense bluish-violet coloration is obtained, which rapidly fades, leaving the solution colourless. Should, however, as little as 2 per cent. of antipyrine be present, a permanent bluish-green coloration is visible after the violet colour due to the pyramidone has faded away.

The method described for the estimation of antipyrine is based on the precipitation of this substance by means of formaldehyde. One gram of the sample is treated with 5 c.c. of water, 5 c.c. of hydrochloric acid, and 2 c.c. of a 40 per cent. formaldehyde solution. After four hours, the precipitate which is obtained if antipyrine is present is collected on a small filter, washed with cold water, dried, detached

from the filter, and weighed. The weight of this precipitate represents from 90 to 100 per cent. of the antipyrine present in the sample. The pyramidon in the filtrate may be obtained by shaking out the latter with chloroform and evaporating the chloroform solution at a low temperature. The method gives approximate results. W. P. S.

Alkaloid Reactions. C. REICHARD (*Chem. Centr.*, 1905, ii, 172; from *Pharm. Zeit.*, 50, 430—431. Compare this vol., ii, 561, 563).—*Quinine and Cinchonine*.—Some new tests are given for these alkaloids, of which the following are the most characteristic. If quinine sulphate is mixed with powdered ammonium persulphate and the mass carefully moistened with hydrochloric acid, a beautiful green coloration appears, whilst cinchonine is as a rule unaffected. On adding to the acid mixtures a drop of strong potassium thiocyanate, both alkaloids give a dirty-green coloration with a shade of red, which soon changes into yellow. If a mixture of quinine sulphate, potassium ethyl sulphate, and potassium ferrocyanide is heated to incipient fusion, no change is noticed, but in the case of cinchonine the mass becomes a dark blue. If potassium ethyl sulphate is heated with quinine sulphate and hydrochloric acid and then mixed with potassium thiocyanate, no reaction is noticed on introducing into the liquid a clear crystal of potassium ferrocyanide, but with cinchonine sulphate the crystal becomes a fine ruby-red; this reaction, however, is not always successful. If a mixture of quinine sulphate and sodium picrate is moistened with a drop of water and then dried, the mass on being moistened with a drop of concentrated potassium thiocyanate solution assumes a splendid and permanent orange-red colour; cinchonine only gives a passing faint orange coloration. L. DE K.

Estimation of the Active Principles of Alder Bark and Cascara Sagrada and their Extracts. JULES WARIN (*J. Pharm. Chim.*, 1905, [vi], 22, 12—14).—The method previously described (*Abstr.*, 1905, ii, 363) for the examination of alder bark is not applicable to *Cascara sagrada*, as the latter contains hydroxymethylanthraquinone compounds which are not directly soluble in alkaline solutions. The powdered bark must be heated for two hours with 2 per cent. sulphuric acid at a temperature of 100°, cooled, extracted (powder and solution) many times with ether, and the united ethereal solutions shaken out with 2 per cent. sodium hydroxide. The alkaline solution obtained serves for the colorimetric estimation as described for alder bark. These methods may be also used for the analysis of the extracts of the above-mentioned barks. Alder bark was found to contain 3.5 per cent. of active principle (as emodin) and the extract 0.755 per cent., whilst *Cascara sagrada* containing 0.605 per cent. of emodin yielded bitter and non-bitter extracts containing 0.590 and 0.595 per cent. respectively. W. P. S.

Easy Way of Distinguishing English from Chinese Rhubarb. ALEXANDER TSCHIRCH (*Chem. Centr.*, 1905, ii, 82—83; from *Schweiz. Woch. Pharm.*, 43, 253—254).—English rhubarb (*Rheum Rhaponticum*) is distinguished from the Chinese variety by containing a well-

crystallised glucoside *rhaponticin* insoluble in ether. Ten grams of the suspected root are boiled for 15 minutes with 50 c.c. of dilute alcohol, the filtrate is concentrated to 10 c.c., and when cold it is shaken with 10—15 c.c. of ether. The extract from truer rhubarb is still clear after 24 hours, but if the *Rhaponticum* variety has been substituted a decided deposit of prismatic needles will have formed. These crystals may be further identified by moistening with sulphuric acid, which produces a purple coloration changing to orange. L. DE K.

Beer Analysis by means of the Refractometer. GEORG BARTH (*Chem. Centr.*, 1905, i, 1747; from *Zeit. ges. Brauw.*, 28, 303—306).—If x represents the amount of alcohol, y the amount of extract in a beer, r the refraction difference, and s the difference in sp. gr. of the beer and water, we have: $x = 003366r + 0.001303s$. $y = 0.007598r - 0.002923s$. The correctness of these formulæ was fully confirmed. L. DE K.

Estimation of Extract in Malt. C. BLEISCH and P. REGENSBURGER (*Chem. Centr.*, 1905, i, 1747; from *Zeit. ges. Brauw.*, 28, 313—316).—A slight modification of the usual process. The malt is mashed as usual, and when saccharification has set in, the whole is boiled over an asbestos millboard for twenty minutes. When cooled to 65°, 10 c.c. of a fresh green malt extract are added and the whole is kept at 65—70° for ten minutes. L. DE K.

Estimation of Bacillus Coli in Potable Waters. ALBERT GAUTIÉ (*Ann. Chim. anal.*, 1905, 10, 254—257).—The author has made a slight modification in the usual process for the detection of the *Bacillus coli communis* in waters. This method, as is well known, consists in adding peptone-broth and a sufficient amount of phenol to prevent the growth of a large number of saprophytic germs. Instead of using 100 c.c. of water, the author makes repeated experiments with 100, 80, 50, 20, 10, and 1 c.c. of water, then further trials with 20, 10, 5, and 1 drops of the sample. It is only by such repeated experiments that a fair idea may be obtained as to the quantity of the coli-bacilli. The mere presence of the bacillus is not sufficient to condemn a water. For further details the original paper should be consulted.

L. DE K.

General and Physical Chemistry.

Determination of Refractive Indices of Hydrogen, Carbon Dioxide, and Oxygen in the Infra-red. JOHN KOCH (*Ann. Physik*, 1905, [iv], 17, 658—674).—An interference method is employed and details are given. For hydrogen for a wave-length = 8.69μ , the value 1.0001373 at 0° and 760 mm. was obtained, a result in accord with the value 1.000264 obtained by Boltzmann for the dielectric constant. From the values of the refractive index for this and other wave-lengths, the author deduces by Drude's equations (*ibid.*, 1904, 14, 677 and 936) the value 1.49×10^7 for the ratio e/m . For carbon dioxide for the same wave-length, the value 1.0004578 was obtained; this is greater than that for the D-line, so that the gas furnishes a case of anomalous dispersion. For oxygen, the value found was 1.0002661, which is less than the values hitherto obtained for the lithium and D-lines (1.000271), so that the dispersion is normal. L. M. J.

Relation between Electrolytic Dissociation and Refractive Power. FILIPPO ZECCHINI (*Gazzetta*, 1905, 35, ii, 65—86).—The author has made a large number of measurements of the densities and refractive indices for sodium light and at the ordinary temperature of solutions of different concentrations of sulphuric, hydrochloric, nitric, acetic, propionic, trichloroacetic, phosphoric, phosphorous, and hydrofluoric acids, sodium and potassium hydroxides, ammonia, potassium nitrate, chloride, acetate, and trichloroacetate, and ammonium nitrate. The numbers obtained lead to the following conclusions.

The dissociation of sulphuric acid by dilution with water effects only a very small change in the molecular refraction of the acid. With hydrochloric and nitric acids, the molecular refraction increases slightly with the dilution. The increase scarcely ever amounts to 2.2, which should be the value corresponding with the complete ionisation of a hydrogen atom. Leblanc and Rohland's hypothesis, according to which the hydrogen ion has double the refraction of the hydrogen atom, is therefore regarded by the author as not justified, the small deviations of the molecular refraction being equally well attributable to the anion. The values obtained for solutions of the bases examined indicate no difference in refraction between a hydroxyl group and a hydroxyl ion.

In the case of salts, the molecular refraction is mostly independent of the concentration of the solution.

The molecular refraction of the water formed in the neutralisation of an acid by a base varies considerably. For the strong acids (nitric, hydrochloric, sulphuric, and trichloroacetic) with the strong bases, potassium and sodium hydroxides, it varies from a minimum of 7.71 with sodium sulphate to a maximum of 8.40 with potassium trichloroacetate, whilst it has the value 5.97 for ammonium nitrate or potassium acetate. No explanation is advanced for these divergences.

Further researches are necessary before definite conclusions can be arrived at concerning the influence of dissociation on refraction, the views of Ostwald and Leblanc not being confirmed by the results already obtained.
T. H. P.

Chemiluminescence. MAX TRAUTZ (*Zeit. physikal. Chem.*, 1905, 53, 1—111. Compare Trautz and Schorigin, this vol., ii, 494; also Guinchant, *ibid.*, 366; Gernez, *ibid.*, 430, 431).—The paper contains an exhaustive historical and critical review of the observations made on crystalloluminescence, triboluminescence, and reaction luminescence. Many new cases of crystalloluminescence have been observed, and attention is drawn to the fact that this phenomenon may accompany the separation of crystals from fused masses. The author considers that crystalloluminescence is essentially the same phenomenon as triboluminescence (see Trautz and Schorigin, *loc. cit.*). Of 285 inorganic substances examined by the author or earlier workers, 33 are found to be triboluminescent; of 147 aliphatic compounds 30, of 305 aromatic compounds 112, are found to be triboluminescent; of 90 alkaloids and alkaloid derivatives, as many as 63 are triboluminescent. There are certainly some cases at least of triboluminescent substances which do not exhibit physical isomerism of any sort. A large number of reactions was examined for reaction luminescence, and this phenomenon was observed specially in cases where oxygen or the halogens were the active agents. It was found that increase of the reaction velocity, and whatever contributed to this, increased the intensity of the luminescence. The spectrum of the light emitted in cases of crystalloluminescence and reaction luminescence is continuous even with luminescent gases, as, for example, in the cold (50—90°) acetylene-chlorine and acetylene-bromine flames.
J. C. P.

Atmospheric Electricity [Radioactivity] in High Latitudes. GEORGE C. SIMPSON (*Phil. Trans.*, 1905, A, 205, 61—97).—This paper records results of observations made in Lapland, and part of it deals with the influence of the wind, the humidity, the height of the barometer, &c., on the atmospheric radioactivity. The observations give strong support to Elster and Geitel's view that the emanation in the air originates from the radium or radioactive emanation in the soil. Anything which tends to reduce the atmospheric circulation tends also to increase the quantity of emanation in the lower layers of the atmosphere.
J. C. P.

Radioactivity of Atmospheric Precipitations and of Surface Waters. JOSEF JAUFMANN (*Chem. Centr.*, 1905, ii, 600; from *Meteorol. Zeit.*, 22, 102—113).—A measured amount of potassium alum solution is added to 1 litre of the water under examination and precipitated with ammonia. The radioactivity of the emanation and the induced radioactivity, which are all collected in the precipitate, are determined together in an apparatus resembling that of Elster and Geitel, and are found generally to lie between the activity of radium and that of thorium. Rain is always slightly active, most so that collected during a thunderstorm in the spring, or in a town; the activity diminishes as the rain shower continues; freshly fallen snow is 3—5

times as active; rain and snow diminish in activity after they have fallen, but snow on the ground may be reinforced by further absorption. The radioactivity of hailstones is greater than that of rain. Natural ice also is sometimes strongly radioactive.

Surface water is always radioactive, but the values vary enormously and seem to depend on the atmospheric pressure. This applies also to spring waters; the deepest spring is most radioactive. If the ground is frozen for long, the radioactivity increases, and diminishes again after a thaw.

G. Y.

Production of Radium from Uranium. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1905, [iv], 20, 239—244. Compare Abstr., 1904, ii, 666).—The author considers that the conclusions drawn by Soddy from his experiments on the production of radium are unjustifiable. With a view to determining whether it is possible to observe the formation of radium in a uranium solution, 250 c.c. of a solution containing 100 grams of "purest uranium nitrate," which had been recrystallised five times, were introduced into a glass bulb of 400 c.c. capacity, the neck of which was then drawn out and sealed. Thirty days later, the entire gaseous contents were removed and transferred to an electroscope, and in order to displace the dissolved gases and any radium emanation the solution was boiled for fifteen minutes. The electroscope was capable of detecting 1.7×10^{-11} gram of radium, but no increase in the normal leak of the instrument could be detected. Similar negative results were obtained at the end of six months and of 390 days. It can be positively asserted that in 390 days the quantity of radium produced from 48 grams of uranium in a uranium nitrate solution is less than 1.7×10^{-11} gram. This is less than one-sixteen-hundredth of the quantity which would be expected from the disintegration theory if the value of λ for radium is taken as $8.8 \times 10^{-4}(\text{year})^{-1}$. The experiments indicate that one or more products of a slow rate of change intervene between uranium and radium.

H. M. D.

Properties of Radium in Small Quantities. A. VOLLER (*Chem. Centr.*, 1905, ii, 388; from *Physikal. Zeit.*, 1905, 6, 409—411).—A reply to Eve (this vol., ii, 367).—The author has repeated his experiments with some modifications and again finds the intensity of radiation is not proportional to the quantity of radium; if the latter is reduced to one-millionth of its original amount, the fall of potential produced by it is only reduced to one-three-hundredth. The same amount of radium spread over ten times the area produces 4 or 5 times as great a fall of potential as before. The suggestion is put forward that the breakdown of radium bromide can be retarded by the presence in the surrounding air of the products of decomposition. Rutherford's suggestion (this vol., ii, 367) that solid radium bromide volatilises is not regarded as probable, inasmuch as an active plate hardly ever loses its activity. The author maintains that radium compounds decompose more rapidly at the surface than at lower layers.

P. H.

Scintillations produced by Radium. ROBERT W. WOOD (*Phil. Mag.*, 1905, [vi], 10, 427—430).—Different interpretations have been given of the scintillations at a zinc sulphide screen caused by the bombardment of radium corpuscles. According to Crookes, each flash is due to the impact of a positive α -particle; according to Becquerel, the production of light results from cleavage of the crystals, brought about by the action of the rays. The author has determined the duration of (1) the spinthariscopes flashes, (2) the flashes produced by cleavage, that is, the triboluminescence. It appears that the duration of (1) is between $1/15,000$ th and $1/20,000$ th of a second, much shorter than that of (2). Hence it is probable that the two phenomena are not very closely related. A photographic examination of the scintillations shows that only a small percentage of zinc sulphide crystals becomes luminous under the radium rays. It is known that the phosphorescent power of most substances is due to minute traces of impurity, and hence a scintillation probably occurs only when an electron strikes a molecule of the impurity. This would do away with the difficulty involved in Crookes' view, for the actual number of α -particles emitted from the radium must far surpass the number of flashes of light as seen in the spinthariscopes. J. C. P.

Slow Transformation Products of Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1905, [vi], 10, 290—306. Compare Abstr., 1904, ii, 799).—Further experiments on the variation of activity of the successive products of radium have been made, and a new product, previously overlooked, has been isolated.

At the end of twenty-four hours the products, radium-A, -B, and -C, which are formed on a plate exposed to radium emanation, have been almost completely transformed, but there is a small residual activity comprising both α - and β -rays which is in general of the order of one-millionth of the activity immediately after removal.

The β -ray activity increases with time according to the equation $I = I_0(1 - e^{-\lambda t})$, and reaches a practical maximum after about forty days. Half the final activity is attained in six days and the constant $\lambda = 0.115(\text{day})^{-1}$. The α -ray activity also increases and reaches half its final value in about 143 days.

The explanation of the experimental results is that the primary product, radium-D, does not emit either α - or β -rays; it undergoes slow transformation (half complete in forty years) with the formation of a product, radium-E, which emits β - and probably γ -rays, and this β -ray product is the parent substance of a product, radium-F (previously termed radium-E), which emits only α -rays.

By heating a platinum plate coated with the active deposit at 1000° , radium-F and the greater part of radium-D are volatilised. The activity of the residual radium-E decreases exponentially with the time and reaches half value in 4.5 days. The difference between the transformation periods deduced from the recovery curve and the decay curve is attributed to an alteration in the radium-E after exposure to the high temperature.

When a bismuth plate is introduced into solution of the active

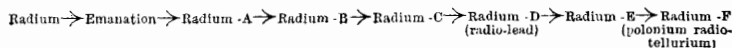
deposit, radium-F is deposited and separated from radium-D and -E. The activity of the deposit decays exponentially and reaches half value in 143 days [$\lambda = 1.77(\text{year})^{-1}$].

From the agreement in the chemical and physical properties of radium-F and radiotellurium and the equality of their decay constants, there can be little doubt about the identity of these two substances. It is calculated that a ton of mineral containing 50 per cent. of uranium contains 0.14 mg. of radium-F, and this number agrees closely with the amount of radiotellurium extracted by Marckwald from uranium residues. Assuming that the α -particles from radium and radium-F produce about the same amount of ionisation, the activity of radium-F in the free state should be about 3200 times the activity of pure radium at its minimum activity, which also agrees with Marckwald's observations on the activity of radiotellurium.

The published observations on polonium indicate the presence of impurities, but there can be little doubt that the chief constituent of polonium is identical with radium-F.

Some experiments with a sample of radio-lead, four months old, showed that the β -ray activity was constant during six months, whilst the α -ray activity steadily increased. These, and the observations of Hofmann, Gonder, and Wölfl (this vol., ii, 71) on radio-lead, seem to indicate that old radio-lead consists of radium-D, -E, and -F, whilst a freshly prepared specimen is probably represented by radium-D.

The entire process of disintegration of radium according to present data corresponds to the following scheme :



Time for half transformation :

1300 years 4 days 3 mins. 21 mins. 28 mins. 40 years 6 days 143 days

Ray emission :

α α α — α, β, γ — β, γ α

No evidence of further transformation has been obtained. If the α -particle is a helium atom, then, since five products emitting α -particles are present in radium, the atomic weight of the transformation product should be $225 - 20 = 205$. This number is very nearly equal to the atomic weight of lead, and the view that lead is the end-product of the series is supported by the fact that lead is always present in the radioactive minerals in about the amount to be theoretically expected from the content of uranium when the quantity of helium present is used to compute the age of the minerals.

H. M. D.

Some Properties of the α -Rays of Radium. HENRI BECQUEREL (*Compt. rend.*, 1905, 141, 485—490).—A reply to Bragg and Kleeman and to Rutherford (compare Becquerel, *Abstr.*, 1903, ii, 256, 257, 402, 523; 1904, ii, 6; Bragg and Kleeman, this vol., ii, 5; Rutherford, this vol., ii, 495).

M. A. W.

Decomposition of Water by Radium. Sir WILLIAM RAMSAY (*Meddel. k. Vet. Akad. Nobel inst.*, 1905, 1, 909—911).—It has been

found by various observers that the gas evolved by decomposition of water by means of radium bromide contains an excess of hydrogen. Various causes are suggested to which this might be due, one of which, namely, oxidation of grease of stopcocks, &c., is of frequent occurrence. When this is avoided, it is found that neither free bromine nor ozone is produced, that it does not seem probable that hydrogen is evolved from radium itself, and that no hydrogen peroxide or radium bromate is formed. In the presence of the emanation, however, dry oxygen is found to oxidise the mercury, and when the emanation acts on pure water with no oxidisable substance present, the gases produced consist wholly of the explosive mixture of oxygen and hydrogen. The action must be attributed wholly to α -rays, as β -rays are without action. L. M. J.

Absorption of the β - and γ -Rays of Actinium. T. GODLEWSKI (*Phil. Mag.*, 1905, [vi], 10, 375—379. Compare this vol., ii, 497, 498).—The penetrating power of the β -rays of thorium and radium increases with the thickness of matter traversed, whereas the β -rays of actinium are homogeneous, and absorption takes place according to the exponential equation $I = I_0 e^{-\lambda x}$, where x is the thickness of matter traversed.

The penetrating power of the β -rays of actinium is only about 40 per cent. of that of the uranium rays, and about one-third of the average penetrating power of the β -rays of radium.

Experiments with different metals show that the deviations from the absorption density law ($\lambda/d = \text{constant}$) are considerably smaller than in the case of the other radioactive elements. The thickness of metal required to absorb half the rays and the absorption constant has been determined.

	Aluminium.	Mica.	Brass.	Copper.	Tinfoil.	Lead.
Thickness (mm.).....	0.212	0.21	0.065	0.063	0.045	0.0425
λ cm. ⁻¹	32.7	33.0	108.0	139.0	154.0	163.0
λ/d	12.9	12.0	13.1	15.9	15.7	14.1

The absorption of the γ -rays of actinium follows an exponential law. These rays also have a very small penetrating power compared with the γ -rays of other radioactive elements, for example, only about one-tenth of that of the more penetrating γ -rays of radium. For iron, zinc, and lead, the thickness of metal required to absorb half the rays is 5.70, 5.60, and 1.92 mm., and the absorption constants 1.23, 1.24, and 4.54 respectively.

H. M. D.

Determination of Wave-lengths in the Spectrum of Giesel's Emanium. J. HARTMANN (*Chem. Centr.*, 1905, ii, 388; from *Physikal. Zeit.*, 1905, 6, 401—402).—In addition to the line previously described at $488.5\mu\mu$, the spectrum comprises the following: two bands, one brighter at $356\mu\mu$, the other weaker at $434\mu\mu$; two very faint, fine lines, $413.7\mu\mu$ and $474.3\mu\mu$ respectively; an indistinct double line ($527.2\mu\mu$ and $530.6\mu\mu$?), and two very faint lines, $570.4\mu\mu$ and $583.8\mu\mu$. Traces of impurity, such as a mechanically retained gas or a solid substance in solid solution, might conceivably

become luminous through the radiation of the emanation, as is the case, described by Giesel, of the addition of didymium to lanthanum chloride. It has, however, not yet been proved whether the spectrum just mentioned is identical with that of didymium or not. It is noteworthy that a substance which is luminous at low temperatures without external supply of energy should give a spectrum with well-defined lines, and having a maximum in the ultra-violet region.

P. H.

Generator Gas- and Carbon-cells. FRITZ HABER and ALEXANDER MOSER (*Zeit. Elektrochem.*, 1905, 11, 593, 609).—The lower end of a test-tube is etched inside and outside with hydrofluoric acid, the roughened surfaces moistened with platinic chloride and heated so as to produce a coating of spongy platinum; electrical contact is made to the coatings by means of platinum wires, and suitable tubes are introduced to allow of carbon monoxide, oxygen, or other gases being brought into contact with the platinum coatings. The whole is heated by a jacket of boiling sulphur on phosphorus pentasulphide. The hot glass itself acts as the electrolyte, the two coatings of platinum being the electrodes. In most of the experiments the outer coating was in contact with air, a mixture of carbon dioxide with a little carbon monoxide or pure oxygen being passed into the inside of the tube and the difference of potential between the electrodes measured. A discussion of the thermodynamics of the reaction $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$ leads to the following expression for the free energy A :

$A = 67440 - 2.42T \log T + 0.0017T^2 - 4.56T \log_{10} p_{\text{CO}_2}/p_{\text{CO}} \times p_{\text{O}_2}^{\frac{1}{2}} - 5.95T$. From this the *E.M.F.*'s at the absolute temperatures 717° and 791° are easily calculated by substituting the values of T and dividing by 46220. The partial pressures of the reacting gases are used in place of their concentrations. The differences of potential measured are well defined and easily reproduced. At the temperature of boiling phosphorus pentasulphide, a mixture of 96.1 per cent. CO_2 and 1.6 per cent. CO , measured against oxygen, gave 0.944 to 0.975 volt, the calculated value being 0.964 volt. In sulphur vapour, a mixture of 97.8 per cent. CO_2 and 1.71 per cent. CO gave 1.012 volts, the calculated value being 1.013 volts. It is also shown that variations in the concentration of the carbon monoxide or of the oxygen produce changes in the *E.M.F.* which agree in sign and very nearly in magnitude with those required by the theory. When pure carbon monoxide is used, it decomposes in presence of the platinum, depositing carbon. This deposit of carbon produces an *E.M.F.* (of nearly 1 volt). That the *E.M.F.* is due to the carbon is proved by the fact that it persists in presence of carbon dioxide, but disappears if oxygen is passed in. In conclusion, an experiment was made with hydrogen and oxygen in the same apparatus. The *E.M.F.* measured varied from 1.183 to 1.196 volt, the calculated value being 1.153 volt.

The resistance of a carbon monoxide-oxygen cell, constructed in the way described, is about 500 ohms; when closed through an external resistance of 10,000 ohms, a current is produced which at first rapidly diminishes; after a minute it reached the value 0.32×10^{-4} ampere: the *E.M.F.* of the cell had fallen to 0.26 volt. T. E.

Mean Potential at Electrodes under the Action of Alternating Currents. PHILIP GEORGE GUNDRY (*Zeit. physikal. Chem.*, 1905, 53, 177—212).—A theoretical and physical paper. The author has made experiments in which an alternating current of varying frequency was sent through an electrolyte between two mercury electrodes, the one very small, and the other so large that it could be regarded as unpolarisable in comparison with the smaller. The effects observed were (1) an alteration of the direct current or of the *E.M.F.*, (2) an alteration of the surface tension of the mercury. The first effect may be due to (a) the asymmetry of the polarisation, or (b) the partial transport of the cathodic component of the current by hydrogen. When a typical salt is taken as the electrolyte, (a) is masked by (b). With complex salts, especially those giving an alkaline reaction, (b) is negligible, and the result of (a) is evident. J. C. P.

Chemical Transfer of Metallic Potentials. ROBERT LUTHER (*Zeit. physikal. Chem.*, 1905, 52, 626—628).—Critical remarks on Fischer's recent paper (this vol., ii, 501). The author points out that several years ago he made experiments similar to some of Fischer's (see Abstr., 1901, ii, 301). J. C. P.

Temperature-coefficient of Electrical Resistivity of Carbon at Low Temperatures. H. MORRIS-AIREY and E. D. SPENCER (*Mem. Manchester Phil. Soc.*, 1905, 49, [x], 1—8).—The measurements were made with carbon filaments taken from Ediswan incandescent lamps. The filament, together with a platinum resistance thermometer, was suspended centrally in a thick brass cylinder surrounded by a Dewar tube. After initial determination of the resistance with the filament and thermometer immersed in liquid air, this was poured out and a series of measurements was made during the steady rise of temperature, which was comparatively slow on account of the considerable heat capacity. The resistance of the carbon increases uniformly as the temperature falls until -150° is reached, when the rate of increase over a small interval of temperature is smaller; at -182° , however, the resistance has increased to a value which corresponds almost exactly with that calculated by extrapolation by means of the constant temperature-coefficient. A readjustment of the relative positions of the particles is suggested as the cause of the observed irregularity. A table of specific resistances between -197° and -4° is appended. H. M. D.

Disruptive Discharge in Gases at High Pressures. CH. EUG. GUYE and H. GUYE (*Arch. Sci. phys. nat.*, 1905, 20, 111—123).—The potential difference necessary to produce the disruptive discharge for a definite distance was determined for various gases at different pressures. It was found that between 1 and 10 atmospheres the potential is a linear function of the pressure; at higher pressures, the ratio of potential to pressure diminishes. In the case of nitrogen, the curve

exhibits a maximum in the neighbourhood of the pressure of maximum compressibility. The experiments with air similarly showed a slight rise in the curve for $p=65$ metres of mercury. Experiments with carbon dioxide in the neighbourhood of the critical point indicated a lowering of the explosion potential, but the experiments are complicated by the partial decomposition of the gas. Little or no effect was found to result from the presence of salts of radium or the influence of X-rays.

L. M. J.

Glow Discharge in Vapours of the Mercuric Haloids. W. MATTHIES (*Ann. Physik*, 1905, [iv], 17, 675—693).—Work on the potential gradient in gases at low pressure has been largely confined to nitrogen; the author has extended investigations of this nature to the vapours of mercuric chloride, bromide, and iodide. He finds that the glow discharge in these gases does not differ from that in the elementary gases, and verifies the absence of any noticeable decomposition with suitable current and platinum electrodes. Copper, iron, aluminium, and mercury cause decomposition without current. The potential gradients are considerably higher than that for nitrogen, as are also the cathode and anode falls. The gradient increases with pressure at first more rapidly, later more slowly than the latter. The dependence on current strength appears very complicated, differing for different pressures; the gradient also decreases with increasing cross-section of the tube. The cathode fall increases approximately as the molecular weight of the compound.

L. M. J.

Conductivity of Sulphuric Acid at Different Temperatures. BLAS CABRERA FELIPE (*Chem. Centr.*, 1905, ii, 438—439; from *Physikal. Zeit.*, 1905, 6, 422—429).—The composition of the solutions, which vary from 2.66 to 35.34 mols. of water per mol. of sulphuric acid, was determined by measurement of their densities at 15°. The conductivity temperature curve is convex towards the temperature axis at high concentrations and concave at low concentrations. With increasing dilution, the point of inflection is displaced more and more towards the lower temperatures. The existence of these points is explained by the antagonistic influence of the temperature on the mobility and on the degree of dissociation. If the conductivity at each temperature be expressed as a function of the concentration, the conductivity maxima appear most sharply defined at high temperatures. Occasionally two maxima are observed, but the author is not convinced of the existence between these of a minimum corresponding with 14 mols. of water per mol. of acid.

P. H.

Electrical Conductivity of Potassium and Sodium Nitrates and of Fused Mixtures of the Two Nitrates together and with other Salts. ALEXIS BOGORODSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 760—807).—The author has determined the specific electrical conductivities of fused potassium and sodium nitrates and various mixtures of the two salts at different temperatures, the results being given in reciprocal ohms in the following table:

Temperature.	Per cent. by weight of potassium nitrate.						
	100.	94·392.	73·224.	54·323.	49·386.	14·493.	0.
348°	0·639	0·662	0·751	0·830	0·848	1·045	1·122
351	0·649	0·671	0·760	0·843	0·857	1·048	1·137
354	0·658	0·680	0·770	0·854	0·866	1·055	1·152
357	0·667	0·689	0·779	0·865	0·877	1·067	1·166
360	0·676	0·699	0·787	0·875	0·888	1·088	1·179
363	0·685	0·709	0·796	0·885	0·901	—	1·192

The conductivities of these mixtures are smaller throughout than the numbers calculated additively.

The author has also examined the effect on the specific conductivity of fused sodium nitrate of admixtures of a number of other salts in varying proportions. Lithium chloride causes a slight increase in the conductivity of sodium nitrate, but all the other salts experimented with diminish the conductivity. The results are given in detail.

T. H. P.

Use of Balanced Electrodes. W. W. HALDANE GEE (*Trans. Faraday Soc.*, 1905, 1, 237—250).—Several forms of balance voltmeters are described for measuring quantities of electricity with a degree of accuracy sufficient for commercial purposes. In one of these, the cathode is suspended in a solution of a salt of the metal to be deposited from one of the pans of an ordinary physical balance. Before starting, the cathode is accurately counterpoised; the current is then passed, and the increase in weight of the cathode is determined. With copper, zinc, silver, and mercury, satisfactory results were obtained. In a second form of apparatus, a hydrometer constructed of thin brass is employed as a combined cathode and balance, and in a third a spring balance arrangement from which the cathode is suspended gives a convenient means of measuring total current flow.

H. M. D.

Very Unequal Electrodes. Valve Cells. Metal Vegetation. W. HOLTZ (*Chem. Centr.*, 1905, ii, 595; from *Physikal. Zeit.*, 6, 480—485).—Currents of varying *E.M.F.* are passed through an electrolytic cell containing an acid or salt solution and two electrodes of the same metal, but of very different sizes. If the direction of the current is changed, the deflection of the galvanometer is almost always altered; with some metals, the deflection is smaller when the small electrode is the anode, but reversely with other metals. The variation in the deflection is greater usually when the concentration of the solution and the *E.M.F.* are smaller. Valve cells, which approach the aluminium cell, are formed with iron, lead, nickel, antimony, and bismuth in 1 per cent. sulphuric acid when the *E.M.F.* is small, but with copper in copper sulphate or chloride when the *E.M.F.* is moderate. Metal trees are formed by copper, zinc, iron, cadmium, and cobalt in addition to

the cases previously known; the branching is most delicate with cadmium, and is fungus-like with cobalt. The cause of the irregularities lies in the smaller electrode on which is formed a layer of oxide or superoxide if it is the anode, or of hydrogen or loose metallic deposit if it is the cathode. G. Y.

The Behaviour of Magnesium Anodes. G. BABOROVSKÝ (*Zeit. Elektrochem.*, 1905, 11, 465—482).—Hydrogen is evolved at a magnesium anode immersed in a neutral solution of a sulphate or chloride and a black substance is formed, which was formerly regarded as a suboxide, but which appears to be a mixture of hydroxide and finely-divided magnesium produced by the pulverisation of the anode. The anode has an apparent valency of about 1.3 which is almost independent of the experimental conditions. A very considerable transition resistance is found at the surface of the anode. By means of a special method the potential of the anode was measured, notwithstanding this resistance, and found to be approximately the same as that of the metal when no current is passing. The latter quantity is very badly defined; referred to Ostwald's zero it is about 1.7 volts.

Attempts to prepare a magnesium suboxide were unsuccessful; the black powder formed at the anode could not be separated from magnesium hydroxide. Magnesium amalgam, when exposed to moist air, rapidly oxidises to a brown, earthy mass from which metallic mercury may be separated by distillation in a vacuum. The residue contains oxides of mercury and magnesium. When a rod of magnesium is immersed in water in contact with copper or platinum, a grey powder is produced which can be partially separated from magnesium hydroxide by suspension in water, but this substance also appears to consist of a mixture of finely-divided metal and hydroxide.

In alkaline solutions, the behaviour of magnesium resembles that of aluminium. An applied *E.M.F.* of 110 volts produces a very small current at first; after some time the temperature rises and a larger current begins to pass; in both cases the magnesium is scarcely acted on and oxygen mixed with about 3 per cent. of hydrogen is evolved. Similar phenomena are observed with lower applied *E.M.F.*'s, but with 2 volts the second stage cannot be observed. During the second stage, the metal dissolves with an apparent valency of about 9. The phenomena may be explained by supposing that a non-conducting layer of hydroxide first forms on the anode; owing to electric endosmosis, this soon dries up, shrinks, and cracks. It is well known that a non-conductor containing fine cracks or pores possesses metallic conductivity. This explains the change from the first to the second stage; the attack of the metal during the second stage is due to portions of the oxide layer falling off and exposing a fresh metallic surface.

In a solution containing both potassium chloride and hydroxide, oxygen and hydrogen are evolved simultaneously at a magnesium anode, and in consequence some anomalous reactions may be observed. In neutral solutions, for example, potassium permanganate and potassium chromate are reduced, whilst iodine is set free from potassium iodide; in alkaline solutions, bromine and iodine ions are oxidised to

BrO_3 and IO_3 ions, permanganate is probably reduced to manganate, whilst chlorine ions are unaltered. T. E.

Cathodic Pulverisation of Tellurium. ERICH MULLER and RICHARD LUCAS (*Zeit. Elektrochem.*, 1905, 11, 521—525).—With an applied *E.M.F.* of 4 volts or more, in pure water, a tellurium cathode loses weight, and yields a colloidal solution of tellurium. The very dilute solutions are reddish-violet in colour, the more concentrated solutions are brown and opaque. The tellurium goes into solution with an apparent valency of about 1.2, which indicates that the pulverisation is not merely mechanical. The dissolution is independent of the presence of oxygen in solution and is therefore not due to oxidation of tellurium hydride. No hydrogen is evolved at the tellurium cathode. The phenomena are analogous to those observed with copper anodes (Abstr., 1903, ii, 587), and may be explained by assuming that the tellurium goes into solution in the form of the ion Te' , which then passes into bivalent tellurium ions either by direct assumption of a second charge from the electrode or by the reaction $2\text{Te}' = \text{Te} + \text{Te}''$.

In alkaline solutions, the pulverisation takes place also, but alkali polytellurides are also formed. In acid solutions, hydrogen is evolved and only a trace of pulverisation can be observed, the discharge potential of hydrogen in the acid solution being lower than that required for the dissolution of tellurium. T. E.

Electrolysis with Alternating Currents. ANDRÉ BROCHET and JOSEPH PETIT (*Ann. Chim. Phys.*, 1905, [viii], 5, 307—345. Compare Abstr., 1904, ii, 229, 230; this vol., ii, 7, 27, 28, 227).—The secondary reactions which take place when platinum dissolves in a solution of barium cyanide under the influence of an alternating current (Abstr., 1904, ii, 229, 414) may be represented by the equations: (1) $\text{Ba}(\text{CN})_2 + 10\text{H}_2\text{O} = \text{Ba}(\text{NO}_3)_2 + 2\text{CO}_2 + 10\text{H}_2$; (2) $\text{Ba}(\text{CN})_2 + 5\text{H}_2\text{O} = \text{BaCO}_3 + \text{CO}_2 + 2\text{NH}_3 + 2\text{H}_2$, and (3) $\text{Ba}(\text{CN})_2 + 2\text{H}_2\text{O} = \text{Ba}(\text{CNO})_2 + 2\text{H}_2$. The third of these reactions may be an intermediate stage in the first.

When iron dissolves in a solution of potassium cyanide under the influence of an alternating current, the cyanide is transformed almost quantitatively into potassium ferrocyanide, but only about 40 per cent. of the hydrogen required by the equation $\text{Fe} + 6\text{KCN} + 2\text{H}_2\text{O} = \text{K}_4\text{Fe}(\text{CN})_6 + 2\text{KOH} + \text{H}_2$ is evolved. This deficiency of hydrogen appears to indicate that the metal dissolves at the anode.

When a solution of sulphuric acid is electrolysed, using platinum electrodes and a combination of alternating and continuous currents (compare Ruer, Abstr., 1903, ii, 407), the platinum slowly dissolves. This appears to be the result of the variation in current density and not to any specific action of the alternating current, since a sinuoidal alternating current obtained from an electrolytic valve of special design produces qualitatively the same effect as a combination of alternating and continuous currents. The platinum also dissolves under the influence of an alternating current in presence of oxidising agents such as nitric acid, chromic acid, &c.

The alternating current appears to exert a specific action in the case

of lead electrodes in dilute sulphuric acid. The metal dissolves and a deposit of lead sulphate, comparatively pure when a current of high density is used and containing reduced lead when a low density current is employed, is formed. The amount of hydrogen evolved varies with the current density and the temperature. With chromic acid in place of sulphuric acid as an electrolyte, reduction occurs and ozonised oxygen is evolved. Phosphoric and arsenic acids behave in much the same way as sulphuric acid, but with them temperature has no influence on the action. The solution of the lead appears to be due to the formation of lead peroxide at the anode, which on the reversal of the current is reduced first to lead sulphate and finally to lead. The reduction of lead sulphate is, however, difficult, especially in the cold, and consequently the sulphate accumulates and the electrode continues to dissolve.

The authors' results show that the alternating current is applicable to many types of reactions, as in the oxidation of ferrous and manganous salts, the reduction of nitric and chromic acids and similar highly oxygenated substances, and to the electrolysis of the hydric acids and their salts. Sulphuric acid, sulphates, chlorates, perchlorates, and chromates appear to be stable towards the alternating current.

The only possible practical application of these results yet observed is the preparation of barium platinocyanide (*Abstr.*, 1904, ii, 414). The memoir concludes with a general discussion and *résumé* of the whole of the results obtained.

T. A. H.

Electrolysis with Alternating Currents. ANDRÉ BROCHET and JOSEPH PETIT (*Zeit. Elektrochem.*, 1905, 11, 441—453. Compare this vol., ii, 27, 28, 227, and 261).—When a current of variable strength (produced by passing an alternating current through an aluminium electrolytic rectifier) is passed through sulphuric acid between platinum electrodes, the anode goes into solution as platinum sulphate, whilst platinum is deposited at the cathode; the deposition at the cathode is prevented or diminished by the presence of oxidising agents such as chromic acid or persulphuric acid; the solution at the cathode is facilitated by small quantities, but diminished by large quantities. The effect of an alternating current is easily understood by means of these results when it is considered that the same electrode is, in this case, alternately anode and cathode. The superposition of a continuous current on an alternating current is shown to be equivalent to the use of a rectified alternating current.

T. E.

Alternate Current Electrolysis. ERNEST WILSON (*Trans. Faraday Soc.*, 1905, 1, 305—312).—Experiments are described in which the effect of an alternating current on plates of lead, zinc, iron, copper, tin, and aluminium immersed in various electrolytes has been investigated. The duration of the action, the frequency of alternation, the current density, and the alteration in weight of the plates are recorded, and curves are appended which show the relationship between the current, the difference of potential between the plates, and the difference of potential between one plate and the electrolyte during

the period of an alternation. For details, the original must be consulted.
H. M. D.

Oxidation and Reduction in the Electrolysis of Solutions of Salts of Iron. Z. KARAOGLANOFF (*Zeit. Elektrochem.*, 1905, 11, 489—496).—The current which just produces an evolution of hydrogen at a platinum cathode immersed in a solution of iron alum in two minutes was found to be proportional to the concentration of the solution; it increases by about 3 per cent. of its value per degree rise of temperature. The addition of some normal salts to the solution increases the value of the critical currents; in the case of copper sulphate, for example, this is due to the deposition of copper at the cathode; other salts have no action and a few diminish the critical currents; among these, the action of the chromates is probably due to the formation of a diaphragm of chromic oxide. With smooth platinum, the critical current is proportional to the surface of the electrode, hence with platinised electrodes very much larger currents can be used. A horizontal cathode gives a larger value than a vertical one. Stirring the solution has a very marked effect in increasing the critical current. A coulometer is constructed on the basis of these results; the anode is enclosed in a porous pot near the surface of the solution of iron alum in which the platinised cathode is immersed and which is stirred by a current of carbon dioxide. The ferrous salt produced is titrated with a solution of potassium permanganate. The mean error of a measurement is +0.23 coulomb.
T. E.

Theory of the Residual Current. WALTHER NERNST and E. S. MERRIAM (*Zeit. physikal. Chem.*, 1905, 53, 235—244).—A rapid and trustworthy determination of the residual current for small $E.M.F.$'s is made possible by the use of a small electrode rotating at a high speed. In those cases where the rate of action of the depolariser is high compared with the velocity of diffusion, the residual current reduces itself to a case of diffusion, and as such may be calculated on the basis of Nernst's theory (see Salomon, *Abstr.*, 1898, ii, 7). The agreement between the calculated and observed values of the residual current is good, and this circumstance is evidence in support of Nernst and Brunner's theory of the velocity of reaction in heterogeneous systems (*Abstr.*, 1904, ii, 315). Where the depolariser acts slowly, the observed values of the residual current are lower than the calculated values, and in these cases the influence of the rate of rotation of the electrode becomes very small. By the method indicated above, it is possible to investigate the residual current for acid-alkali polarisation, and so to arrive at an accurate determination of the neutralisation point.
J. C. P.

Specific Heat of Iron at High Temperatures. JOHN A. HARKER (*Phil. Mag.*, 1905, [vi], 10, 430—438).—The mean specific heat S for the temperature range $0^\circ - T^\circ \text{C.}$ is given in the following table:

<i>T.</i>	<i>S.</i>	<i>T.</i>	<i>S.</i>
200°	0·1175	700°	0·1487
250	0·1204	750	0·1537
300	0·1233	800	0·1597
350	0·1257	850	0·1647
400	0·1282	900	0·1644
450	0·1311	950	0·1612
500	0·1338	1000	0·1557
550	0·1361	1050	0·1512
600	0·1396	1100	0·1534
650	0·1440		

The author considers that the diminution at 900° and the subsequent rise in the specific heat require confirmation. J. C. P.

Molecular Rise of the Lower Critical Temperature of a Binary Mixture of Normal Components. JOHANNES J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 144—152).—The earlier theoretical work (this vol., ii, 434) is revised, and it is found unnecessary to double the molecular formula of sulphur dioxide or of carbon dioxide. An approximate expression for the molecular rise of the lower critical temperature is $1/T_1 \cdot (dT_x/dx)_0 = \theta(\theta - 1)$, where θ is the ratio T_2/T_1 of the two critical temperatures. J. C. P.

Liquid Mixtures of Minimum Boiling Point. CLIFFORD D. HOLLEY and J. T. WEAVER (*J. Amer. Chem. Soc.*, 1905, 27, 1049—1057. Compare Abstr., 1902, ii, 443).—A number of mixtures of liquids have been investigated by the boiling-point method and the following minima have been found: 10 parts of propyl alcohol (b. p. 95·6°) and 90 parts of propyl bromide (b. p. 71·5°) give a liquid with b. p. 69·75°. 16·24 parts of ethyl alcohol (78·4°) and 83·76 parts of propyl bromide give a liquid with b. p. 63·6°. 20·60 parts of methyl alcohol (64·0°) and 79·40 parts of propyl bromide give a liquid with b. p. 54·8°. 19·25 parts of propyl alcohol and 80·75 parts of isobutyl bromide (89·2°) give a liquid with b. p. 86·1°. 41·0 parts of ethyl alcohol and 59·0 parts of isobutyl bromide give a liquid with b. p. 71·4°. With methyl alcohol and isobutyl bromide, a minimum boiling point is obtained at 60°, but this point is not definite, as the mixture may contain from 41 to 56 per cent. of the bromide without any change in the boiling point. 72·0 parts of ethyl alcohol (78·3°) and 28·0 parts of amyl bromide (118·2°) give a liquid with b. p. 77·3°. The addition of as much as 10 per cent. of amyl bromide produces no change in the boiling point of methyl alcohol (64·0°), and further additions cause slight elevations of the boiling point of the mixture. Eight parts of methyl alcohol (64·8°) and 92 parts of methyl iodide (44·5°) give a liquid with b. p. 39·6°. 87·5 parts of bromoform (145·5°) and 12·5 parts of butyric acid (158—159°) give a liquid with b. p. 142·6°. 11·80 parts of propyl alcohol (95·5°) and 88·20 parts of carbon tetrachloride (76·70°) give a liquid with b. p. 72·6°.

Mixtures of carbon tetrachloride with benzene or toluene do not present any unusual phenomena.

The following mixtures show no minimum boiling point: propyl bromide with amyl alcohol or isobutyl alcohol; isobutyl alcohol with isobutylbromide, isobutyl acetate, ethyl butyrate, or amyl acetate; isobutyl bromide with bromoform, amyl acetate, or ethylene bromide; ethylene bromide with bromobenzene or bromoform.

The results of this investigation show that the constitution of the substances has a greater influence on the formation of mixtures with minimum boiling points than the close proximity of their boiling points.

E. G.

Modification of Victor Meyer's Apparatus for the Determination of Vapour Densities. BERNARD J. HARRINGTON (*Amer. J. Sci.*, 1905, [iv], 20, 225—228).—Two modified forms of apparatus are described. In the first, the cylindrical bulb in which vaporisation of the substance takes place is horizontal instead of vertical, and the long stem is bent upon itself a number of times. The second form is similar, but the bulb is in this case vertical. Both forms are very compact, and can be heated in an enclosed box of copper or tinned iron; the construction is, moreover, such that the vapour can be very quickly swept out of the apparatus. Experience has shown that good results can be obtained much more rapidly than with the ordinary form of apparatus.

H. M. D.

Determination of Molecular Weights in Boiling Concentrated Sulphuric Acid. ERNST BECKMANN (*Zeit. physikal. Chem.*, 1905, 53, 129—136).—Results obtained with boron oxide and arsenious oxide indicate that the molecular elevation of the boiling point of sulphuric acid is about 53·3 (in fair agreement with the value calculated from the expression $0\cdot02T^2/W$), and that the formula of the former substance is B_4O_6 . It is further indicated that the formula of molybdic acid anhydride is Mo_2O_6 . The molecular weights obtained for sodium and potassium sulphates are considerably less than the normal values, and it is supposed that the potassium or sodium hydrogen sulphate molecules primarily formed react to produce pyrosulphate. In this connection, it is shown that whilst potassium hydrogen sulphate dissolved in concentrated sulphuric acid has an abnormally high molecular weight, the values obtained for sodium and potassium pyrosulphates are nearly normal.

J. C. P.

Vapour Current Method for the Determination of Molecular Weights at High Temperatures. ERNST BECKMANN (*Zeit. physikal. Chem.*, 1905, 53, 137—150).—A number of detailed modifications are suggested in the apparatus previously described (*Abstr.*, 1902, ii, 303; *Abstr.*, 1903, ii, 533; see also Walther, *Abstr.*, 1904, ii, 234). The author points out the advantages possessed by the method of direct heating as compared with the method of heating by a current of the vapour.

J. C. P.

Elimination of Thermometer Lag and Casual Loss of Heat in Calorimetry. THEODORE W. RICHARDS, LAWRENCE J. HENDERSON, and GEORGE S. FORBES (*Zeit. physikal. Chem.*, 1905, 52, 551—568).—In an ordinary calorimetric determination of the heat developed in a reaction, there are two chief sources of error. Firstly, the real maximum temperature is not reached in the calorimeter through loss of heat to the environment; secondly, the thermometer lags, and cannot indicate with sufficient rapidity the changes of temperature in the calorimeter. The first source of error is usually eliminated by Regnault and Rumford's methods, but the second is generally disregarded. The authors show how the lag may be determined for any given thermometer under given conditions, and how a corresponding correction may be introduced in the results of calorimetric work. Further, they point out that the first source of error mentioned may be eliminated by allowing the temperature of the environment to rise simultaneously with that of the contents of the calorimeter. This is done by allowing a suitable chemical reaction (for example, the neutralisation of acid by alkali) to take place in the external bath surrounding the calorimeter. It is found that this method gives more constant results than the older methods involving calculated corrections for the loss of heat. The results obtained by the new method agree with those obtained by the older methods, provided the latter are corrected for the lag of the thermometer. J. C. P.

Thermochemical Studies. Reply to Julius Thomsen. DANIEL LAGERLÖF (*J. pr. Chem.*, 1905, 72, 80—104).—A polemical paper in which the author replies vigorously to criticisms of Thomsen on the author's previous papers (this vol., ii, 435). He criticises the method of deducing an expression to reproduce experimental results and then claiming from the accord of the experiments and the values calculated by the expression that "the high relative accuracy of the experimental data" is indicated (this vol., ii, 437). He indicates many irregularities and discrepancies in Thomsen's results, and shows that by the author's method of calculation the results of Berthelot appear more regular than those of Thomsen. L. M. J.

Calorimetric Measurement of Heats of Combustion. WILHELM JAEGER and HELMUTH VON STEINWEHR (*Zeit. physikal. Chem.*, 1905, 53, 153—165).—The authors discuss certain problems connected with the determination of heats of combustion in a Berthelot bomb, namely, (1) the possible sources of error in the determination of the water equivalent and in the combustion experiments; (2) the correction for heat exchange with the surroundings; (3) the absolute and relative accuracy of the measurements according to present standards; and (4) the influence on the results of the value of the calorie and its variation with temperature. Special and favourable consideration is given to the electrical method of calibrating a calorimeter (see Fischer and Wrede, *Abstr.*, 1904, ii, 468). Platinum thermometers are recommended in preference to mercury ones for calorimetric work. In connection with point (4) above, it is shown that Fischer and Wrede's

numbers are 0.2—0.3 per cent. too high. For other details of the discussion, the original must be consulted. J. C. P.

Heat of Formation of Silicates. D. TSCHERNOBAEFF (*Rev. de Métallurgie*, 1905, 2, 729—736).—The heats of formation of silicates from silica and the metallic carbonate or oxide have been determined by Le Chatelier's method (Abstr., 1895, ii, 305), in which the reacting substances are mixed with wood charcoal in a calorimetric bomb, the temperature reached by the combustion of the carbon being sufficient to cause fusion of the mass. The method of making the necessary corrections is described.

The following results were obtained: $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$ - 27.3 Cal.; the corresponding heats of formation of Ca_2SiO_4 and Ca_3SiO_5 are - 31.0 Cal. and - 36.0 Cal. respectively for 1 mol. of CaO . $\text{SrCO}_3 + \text{SiO}_2 = \text{SrSiO}_3 + \text{CO}_2$ - 35.1 Cal., BaSiO_3 has - 41.0 Cal.; Li_2SiO_3 has - 24.9 Cal.; Na_2SiO_3 has - 30.4 Cal.

$2\text{SiO}_2 + \text{Al}_2\text{O}_3 + 3\text{CaCO}_3 = 2\text{SiO}_2, \text{Al}_2\text{O}_3, 3\text{CaO} + 3\text{CO}_2$ - 101.9 Cal.; $2\text{SiO}_2, \text{Al}_2\text{O}_3 + 3\text{CaCO}_3 = 2\text{SiO}_2, \text{Al}_2\text{O}_3, 3\text{CaO} + 3\text{CO}_2$ - 116.8 Cal.; $2\text{SiO}_2 + \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} = 2\text{SiO}_2, \text{Al}_2\text{O}_3, 2\text{H}_2\text{O}$ (kaolin) + 43.8 Cal.

The heat of transformation of quartz into vitreous silica was found to be - 0.9 Cal., but is too small to be determined with accuracy.

C. H. D.

Heats of Formation of Mixtures and of Non-aqueous Solutions. WLADIMIR F. TIMOFÉEFF (*Chem. Centr.*, 1905, ii, 429—438; from *Izv. Kieff Polytechn. Inst.*, 1905, 1—340).—The author has made a very exhaustive study of the heats of solution of gases and solids in organic solvents, and of the heat developed on mixing together various organic liquids, with the object of determining whether it is possible to connect the heats of formation of solutions and mixtures with the physical and chemical properties of the components. Tables giving the thermal capacities (c) at 20° and their corresponding temperature-coefficients dc/dt show that the greatest values for temperature-coefficient are given by strongly associated substances such as aliphatic alcohols.

Thermal Capacities of Mixtures.—Additive relationships are shown by mixtures of benzene with chlorobutane, chloroform, carbon tetrachloride, carbon disulphide, and acetone, of heptane with chloroform, carbon disulphide, and ethyl acetate, and of acetic acid with toluene, pyridine, and ethyl alcohol; such relationships do not hold for mixtures of chloroform with pyridine, ethyl ether, acetone, and acetic acid, of acetic acid with carbon tetrachloride, nitrobenzene, and aniline, of the fatty alcohols with all other liquids, of benzene with aniline, ethyl acetate, and acetic acid, and of heptane with ethyl acetate. In other words, the first group comprises non-associated or slightly associated liquids which have no chemical action on each other with the notable exception of the mixtures of acetic acid with toluene, pyridine, and ethyl alcohol; the second group, on the other hand, contains chiefly associated liquids, or substances such as chloroform, which have a powerful chemical affinity for most solvents. The extent of the deviation from the additive rule is found to diminish in the case of the fatty alcohols with increasing

molecular weight. It appears from this that in the absence of any association on the part of the molecules of the two constituents the thermal capacity of a mixture is an additive function of the thermal capacities of those constituents.

A table giving the heats of solution of hydrogen chloride and ammonia in methyl, ethyl, propyl, and isobutyl alcohols of varying concentrations shows that in the case of hydrogen chloride the heat of formation varies inversely as the concentration, whereas in the case of ammonia, owing no doubt to association, it varies directly.

The heat developed when liquids are mixed has been measured in the case of 133 pairs of liquids for different proportions of the constituents, and the results are communicated in more than a hundred tables, which have been summarised in one giving the molecular heat of mixture at infinite dilution for 13 substances in 19 different solvents. By the molecular heat of mixture is meant the heat, expressed in Calories, which is developed when one gram-molecule of a liquid is dissolved in x gram-molecules of solvent. The pairs of liquids examined may be divided under the following heads: (1) mixtures of normal non-associated chemically indifferent liquids; (2) mixtures of normal liquids which act chemically on each other; (3) mixtures of associated with normal liquids which have no action on each other; (4) mixtures of associated liquids which react with each other. For a detailed discussion regarding each of these cases, reference should be made to the original paper.

The heats of solution of solids in indifferent solvents at concentrations approximating to saturation are practically the same as their heats of fusion. The heats of solution of 18 organic solids in various solvents are tabulated. From observations on the heats of formation and vapour pressures of mixtures of liquids, it is found that a certain parallelism exists between the two phenomena, although the parallelism is by no means rigid. It has not been found possible to recognise any direct relationship between the surface tension, dielectric constants, and volume changes of mixtures and their heats of formation. In addition to the large amount of material collected with regard to organic compounds, the author has also determined the specific heats of solution of mercuric chloride in various alcohols, and the heats of solution of mercuric chloride and cadmium iodide in methyl and ethyl alcohols, ether, and ethyl acetate.

P. H.

Modification of van't Hoff's Theory of the Depression of the Freezing Point. J. B. GOEBEL (*Zeit. physikal. Chem.*, 1905, 53, 213—224).—Equations are obtained for the vapour pressure curves of water and ice in the neighbourhood of 0° , and these curves are in very close agreement with the experimental results of Magnus, Regnault, and Juhlin. From these equations, with the aid of thermodynamics and on the basis of van't Hoff's molecular theory, the author deduces the relationship $c' = 0.54\Delta - 0.061\Delta^2 + 0.00154\Delta^3$, which is valid for dilute aqueous solutions. In this equation, Δ is the depression of the freezing point, and c' is the concentration (in molecules per litre) of the dissolved substance as it actually exists in the solution. For very small depressions, the foregoing formula becomes the same as the

simple van't Hoff equation, $c' = 0.54\Delta$. It is probable that the author's formula allows more exact conclusions to be drawn regarding the molecular condition of various solutions. Thus it is shown that the degree of dissociation in salt solutions, and seemingly also the degree of association in alcohol solutions, can be determined in fair harmony with the mass action law. J. C. P.

Alteration of Specific Gravity. GEORG W. A. KAHLBAUM and E. STURM (*Zeit. anorg. Chem.*, 1905, 46, 217—310).—The changes of specific gravity which accompany the deformation of metals by drawing, pressing, twisting, and rolling have been studied, and it has been found that there is a change of specific gravity brought about by the external mechanical action alone; it is suggested that the change, which is always due to an expansion, marks the formation of allotropic modifications. The results are summarised as follows:

Metal.	Sp. gr.		
	Before.	After.	
Commercial platinum	21.4320	21.4170	drawn into wire
Pure platinum	21.4403	21.4336	
Platiniridium	21.4938	21.4766	
Gold	19.2602	19.2506	
Aluminium	2.7031	2.6995	
Cadmium	8.6434	8.6397	
Nickel	8.8440	8.7599	pressed into wire
Alloy of Cu—Al	8.2377	8.2237	
Wood's alloy *	9.6735	9.6661	
Alloy IX. *	9.2940	9.2837	
Alloy VIII. *	9.8223	9.7711	wire submitted to torsion
Gold	19.2322	19.2220	
Commercial platinum	21.4284	21.4112	
Pure platinum	21.4312	21.3985	
Platiniridium	21.3309	21.3150	
Nickel	8.8412	8.8273	

* The percentage composition of the three alloys was:

	Bi.	Pb.	Cd.	Sn.	M. p.
Wood's alloy	50.0	25.0	12.5	12.5	65°
Alloy IX.	47.75	18.39	13.31	20.55	71°
Alloy VIII.	52.0	32.0		16.0	96°

D. H. J.

Aqueous Solutions of Fatty Acids. KARL DRUCKER (*Zeit. physikal. Chem.*, 1905, 52, 641—704).—The experimental part of the work involved the determination of conductivity, density, and surface tension for solutions of formic, acetic, propionic, butyric, isobutyric, *n*-valeric, isovaleric, monochloroacetic, dichloroacetic, and trichloroacetic acids, as also the determination of compressibility for solutions of acetic acid and its chlorine derivatives.

A point of maximum density, already well known for mixtures of acetic acid and water, exists also in the case of aqueous solutions of

the higher homologues. It lies at about 50 per cent. acid concentration for propionic acid, at about 30 per cent. for the butyric acids, and at a smaller concentration still for the valeric acids. No maximum could be detected for formic acid or the chloroacetic acids.

The surface tension of the solutions varies markedly with the concentration and with the position of the acid in the homologous series. The temperature-coefficient exhibits a distinct minimum in several cases, but trichloroacetic acid has a distinct maximum value. The values at 25° of the surface tension γ for acetic acid and its chlorine derivatives in the pure state have been obtained by extrapolation, and are as follows: acetic acid, 26.1; monochloroacetic acid, 41; dichloroacetic acid, 37.2; trichloroacetic acid, 36.0. The order of magnitude of the influence of these acids in dilute solution on the surface tension of water is, however, different from that indicated by the foregoing numbers.

In all the four cases studied, the initial value of the compressibility exhibits a minimum when plotted against the concentration of the solutions, although the extrapolated values for the pure substances are very different, namely, acetic acid, 98; monochloroacetic acid, about 47; di- and tri-chloroacetic acids, 59; water, 47.

The experimental results obtained are used to test a number of theoretical deductions. Thus it is shown that, with the aid of the conception of "apparent" critical constants, van der Waals' constants a and b can be calculated for the abnormal associating members of the homologous series of acids, and even for water from the formulæ of Eötvös and of Ramsay and Shields. In the course of these calculations, it is found that of the two van der Waals' formulæ connecting surface tension and critical pressure, the one $\gamma = \pi \text{ const.}$ is the better. On this basis, it is possible to calculate the surface tension of a normal binary mixture. For mixtures, however, of water and fatty acids, and of water and alcohols, there are deviations from the calculated values, these deviations indicating extensive polymerisation of water, both when in the pure state and when mixed with other substances. Evidence of polymerisation in the cases of water and acetic acid was obtained also from a study of the compressibilities; the higher chlorine derivatives of acetic acid, on the other hand, are found to be normal.

From the compressibilities of variously concentrated solutions of the fatty acids, the changes of internal pressure accompanying the solution process have been calculated; when this change of internal pressure is allowed for in the dissociation formula for trichloroacetic acid, the degree of dissociation can be calculated (up to $N/2$ concentration) in good agreement with cryoscopic measurements. J. C. P.

Surface Tension of Inorganic Salt Solutions. CARL FORCH (*Ann. Physik*, 1905, [iv], 17, 744—762).—In consequence of criticisms of Feustel (*ibid.*, 16, 66), the author has redetermined the surface tension of a number of aqueous solutions of inorganic salts by the drop method, and has compared the values with those obtained by other observers. The various discrepancies throughout all series of determinations led him to consider that the knowledge of the surface

tension is far from accurate, and that whilst different methods, or the same method in the hands of different observers, yield such diverse results even fundamental questions cannot be satisfactorily solved.

L. M. J.

Diffusion of Nascent Hydrogen through Iron. ADOLF WINKELMANN (*Ann. Physik*, 1905, [iv], 17, 590—626).—In order to determine the diffusion of nascent hydrogen through iron, an iron tube closed below was used as the cathode of an electrolytic cell. The top of the iron tube was connected to a glass tube divided in millimetres standing in a mercury trough and connected with an air-pump. A solution of sodium hydroxide formed the electrolyte, and the rate of diffusion of the hydrogen produced on the exterior into the interior of the tube was investigated. The effect of internal pressures was examined, and the author finds that the velocity of diffusion is independent of the pressure of hydrogen inside the tube, at least between the limits 0 and 89 cm. of mercury. The velocity was also not affected when the external pressure was reduced from one to one-half atmosphere. The author concludes that the latter fact indicates that the actual pressure of the hydrogen on the outside of the iron tube is not of the same order as the external pressure, and is not less than 58 atmospheres. He, however, considers the independence of internal pressure to indicate probably that the diffusion is of ionic or atomic and not of molecular hydrogen. At constant temperature, the rate of diffusion was found to increase more slowly than the current strength, but to be approximately proportional to the potential difference. The increase with temperature was rapid, and could be given by the expression $D_t = D_0(1 + 0.0455t)$ for constant current, or $D_t = D_0(1 + 0.0561t)$ for constant potential difference. L. M. J.

Solutions of Sugar and Inorganic Salts in Dialysis. PIO BERLI (*Chem. Centr.*, 1905, ii, 796; from *Bull. Assoc. Chim. Sucr. Dist.*, 22, 1155—1162).—The dialysing power of a 10 per cent. sugar solution increases more quickly than the temperature and solubility. In solutions containing 1 per cent. of a salt (K_2CO_3 , KNO_3 , KCl , Na_2SO_4 , $CaCl_2$), the sugar dialysed the less the greater the amount of dialysed salt. Similar results were obtained with solutions containing 15 per cent. of sugar and 5 per cent. of salt, or 5 per cent. of a mixture of equal amounts of each salt. Dialysing power diminishes as the molecular weight and molecular volume increase. N. H. J. M.

Strong Sterilisable Dialysing Membrane. HIBBERT W. HILL (*J. Amer. Chem. Soc.*, 1905, 27, 1058—1060).—The membrane described is made by sewing together pieces of closely woven silk so as to form the desired shape and immersing this in a hot aqueous solution of gelatin of 20—30 per cent. strength for about 10—15 minutes. The silk is withdrawn, allowed to drain, and then plunged into water at 0° and left for 5—10 minutes, after which it is removed from the water and tested for leaks. If no flaws are found, the gelatinised silk is put into 40 per cent. solution of formaldehyde at 0°, and left

for about a fortnight or until the gelatin has been rendered completely insoluble in hot water. Finally, the membrane is washed or steamed to remove the free formaldehyde.

The membrane thus prepared is very strong, dialyses well, can be repeatedly sterilised with steam or boiling water, and is therefore well adapted for bacteriological work. E. G.

The Clays as Semipermeable Walls. PAUL ROHLAND (*Zeit. Elektrochem.*, 1905, 11, 455—456).—The plastic clays, in the air-dried condition, allow crystalloids to diffuse through them, but not colloids. This property appears to be connected with the presence of inorganic and organic colloidal material in the clay. T. E.

Indifferent Points. PAUL SAUREL (*J. Physical Chem.*, 1905, 9, 556—557).—The temperature (or pressure) of an indifferent point corresponding with a given pressure (or temperature) is a maximum or minimum of the temperatures (or pressures) at which the system can be in equilibrium at the given pressure (or temperature), and the author defines certain conditions in which it is possible to assert whether the temperature will be a maximum or the pressure a minimum (Abstr., 1904, ii, 715). L. M. J.

Thermodynamic Potential and its Application to Problems of Chemical Equilibrium. JOHANNES J. VAN LAAR (*Chem. Centr.*, 1905, 2, 734—735; from *Chem. Weekblad.*, 1905, ii, 427—440).—Several cases of dissociation are considered from the point of view of thermodynamic potential. With the aid of the molecular potentials, Gibbs' formula for the dependence of gaseous dissociation on the pressure and the temperature can be deduced. For details, the original must be consulted. H. M.

Shape of the Sections of the Surface of Saturation Normal to the x -Axis in case of a Three-phase Pressure between Two Temperatures. JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 184—193).—A theoretical paper. J. C. P.

The (T, x) Equilibria of Solid and Fluid Phases for Variable Values of the Pressure. JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 193—195).—A theoretical paper. J. C. P.

Hidden Equilibria in the p - x -Diagram of a Binary System in Consequence of the Appearance of Solid Substances. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 196—200).—Theoretical. J. C. P.

Contribution to the Knowledge of the px - and pT -Lines for the Case that Two Substances enter into a Combination which is dissociated in the Liquid and the Gas Phase. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 200—208).—A theoretical paper. J. C. P.

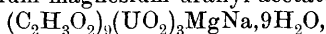
Phenomena observed when the Plait Curve meets the Solubility Curve. ANDREAS SMITS (*Zeit. physikal. Chem.*, 1905, 52, 587—601).—The experiments with ether and anthraquinone (Abstr., 1904, ii, 15) have been extended, and the results support the theoretical views recently advanced (this vol., ii, 234). J. C. P.

Influence of the Solvent on the Equilibrium Constant, and the Relationship between Electric Conductivity and Viscosity. LEO PISSARJEWSKY and N. LEMCKE (*Zeit. physikal. Chem.*, 1905, 52, 479—493).—Part of this work has already been described (this vol., ii, 16). In discussing the effect of adding alcohol or glycerol on the dissociation of potassium chloride and sulphate in aqueous solution, and indirectly on the equilibrium in question (*loc. cit.*), the authors arrive at the view that the degree of dissociation is given by the formula $\alpha = \mu \cdot \eta / \mu_{\infty} \cdot \eta_{\infty}$, where μ and η are molecular conductivity and viscosity respectively. The conductivity and viscosity of solutions of sodium chloride in aqueous glycerol have been determined, and the application of the foregoing formula indicates that the degree of dissociation in aqueous glycerol is greater than in water. With sodium chloride as solute, the value of $\mu_{\infty} \cdot \eta_{\infty}$ is practically the same for each of the three solvents, (1) water, (2) 9.87 per cent. aqueous glycerol, (3) 10.54 per cent. mannitol in water. The degree of dissociation of sodium chloride in mannitol solutions is sometimes greater, sometimes less, than in water. The viscosity of sodium chloride solutions in (1) aqueous glycerol, (2) aqueous solution of mannitol, rises and falls periodically with the dilution. The viscosity of an aqueous solution of sodium chloride between $v=64$ and $v=512$ is smaller than that of pure water, the minimum value being obtained at $v=128$. This is in harmony with Arrhenius' views. J. C. P.

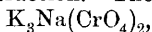
Dineric Equilibria. JAMES M. BELL (*J. Physical Chem.*, 1905, 9, 531—555).—Baneroff has shown that the equilibrium between two non-miscible liquids dissolved in a consolute liquid is expressed by the equation $x^{\alpha}y^{\beta}/z^{\alpha+\beta}=K$ where x , y , and z are the respective concentrations (Abstr., 1895, ii, 157). The validity of this has also been demonstrated by Lincoln (Abstr., 1900, ii, 302). If one or both the liquids are only partially soluble in the third, the expression reduces to $(x+A)^{\alpha}y^{\beta}/z^{\alpha+\beta}=K$ or $(x+A)^{\alpha}(y+B)^{\beta}/z^{\alpha+\beta}=K$. The author has investigated the case where the addition of liquid z to the solution of a solid in liquid 1 caused the precipitation of a liquid phase and not of the solid itself. Assuming this to be an example of the first case, the equation may be reduced to $z^{\eta}/y=K$ if the quantity of solid is kept constant. It is shown that when the solid is a non-electrolyte this expression holds well, the constants having different values for the two liquid phases; when, however, electrolytes were employed, the equation does not hold, as, for example, in the case of potassium carbonate, alcohol, water. It is possible that the lack of accord in such a case is ascribable to dissociation. As the quantity x is not varied, these results do not prove the applicability of the first equation, but indicate that the equilibrium is to be represented by the equation $f(x)y^{\beta}/z^{\gamma}=K$, where the function $f(x)$ is not known.

L. M. J.

Transformation of Polymorphic Substances. HERMANN STEINMETZ (*Zeit. physikal. Chem.*, 1905, 52, 449—466).—A study, with the aid of the dilatometer, of the transition points of a number of substances. Sodium magnesium uranyl acetate,



has a transition point at 27.5° under atmospheric pressure, the change in crystalline character being monoclinic pseudo-hexagonal \rightarrow hexagonal. The transition is not accompanied by any appreciable volume change or heat effect, but the coefficient of expansion becomes less above the transition temperature. Under a pressure of 53 kilos. per sq. cm., the transition temperature is 30° , and the transformation is then accompanied by an expansion of about 0.2 per cent. *iso*Propylamine platinichloride, $(\text{CH}_2\text{Me}_2 \cdot \text{NH}_2)_2, \text{H}_2\text{PtCl}_6$, undergoes at 32° under atmospheric pressure a change from monoclinic pseudorhombic aggregates into definite rhombic crystals. The transformation involves an expansion of about 0.04 per cent., but is unaccompanied by any heat effect. The coefficient of expansion alters as in the case of the uranium compound mentioned above. Under a pressure of 53 kg. per sq. cm., the transition point is 0.5° higher, and the accompanying volume change is slightly less. Other substances have been examined in less detail. Sodium-katapleite, a calcium sodium zirconium silicate, has a transition point at 35° , undergoing a very small change of volume. Tridymite has a transition point at 115° , and its volume expands about 0.6 per cent. Calcium chloroaluminate, $\text{AlO}_3\text{Ca}(\text{CaCl})3\text{H}_2\text{O}, 2\text{H}_2\text{O}$, has a transition point at 35.8° , its volume undergoing a contraction. The double chromate,



undergoes a gradual change between 150° and 175° without appreciable alteration of volume or expansion coefficient. Leadhillite has a transition point at 115° ; the change is monoclinic pseudorhombic \rightarrow rhombic, and is accompanied by considerable expansion. In the case of hexachloroethane, there are two transformations, rhombic \rightarrow triclinic at 45° , and triclinic \rightarrow cubic at 71° . In each case the change is accompanied by a considerable expansion. The transformation of carbon tetrabromide also is accompanied by a marked increase in volume.

J. C. P.

Mixed Crystals in Systems of Three Substances. III. FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1905, 52, 513—550).—A continuation of the earlier papers (this vol., ii, 154, 376).

J. C. P.

Indirect Analyses in Multi-component Systems. WILDER D. BANCROFT (*J. Physical Chem.*, 1905, 9, 558—561).—An extension of a paper on this subject by Browne (*Abstr.*, 1902, ii, 648). If the analyses of a fused mass and of the mother liquor after crystallisation be known, it will probably be found that the ratios of some of the constituents are identical or nearly so. It may be assumed that these have not separated, and if the analyses be referred to unit mass of one of these constituents, the analysis of the separated crystals may be obtained by subtraction of the analysis of the mother liquor from that of the fused mass. Examples are given.

L. M. J.

Foundations of a General Theory of the Electrolytic Solution Tensions of Substances in any Solvent. CARL FREDENHAGEN (*Zeit. Elektrochem.*, 1905, 11, 496—502).—If a partially dissociated binary compound KA in the gaseous condition is acted on by a substance E , the component K will be liberated, no action will occur, or the component A will be liberated, according as the equilibrium constant of the reaction $E + A = EA$ is greater than, equal to, or less than the constant of the reaction $E + K = EK$. It may be assumed that the same thing would occur in the liquid state. Taking water as an example, the elements may be divided into three groups according to whether their affinity for hydroxyl is greater than, equal to, or less than their affinity for hydrogen; group (1) contains the metals, group (2) contains As, B, P, N, C, and group (3) contains the typical non-metals. These groups are electro-positive, neutral, or electro-negative to water. Since reactions in gases are supposed to take place between ordinary molecules and in liquids between charged ions, this connection is not obvious. The author regards the hypothesis of charged ions as unnecessary. Electrolytic dissociation differs from ordinary dissociation in the fact that in the former the products of dissociation are "coupled" and cannot be removed from the system independently of each other. If the temperature of an electrolytic solution be raised gradually past the critical temperature, it passes into a condition of ordinary dissociation, hence electrolytic dissociation is caused by molecular attractions. The fact that "dissociating" solvents all possess large surface tension and large heat of evaporation is in accordance with this. The connection between the affinity of a substance for the dissociation products of a solvent, the molecular forces within the solvent, and the solubility of the substance is also discussed.

T. E.

Application to Electrolytes of the Hydrate Theory of Solutions. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1905, 1, 197—206).—An attempt is made to extend the hydrate theory to electrolytes in such a way as to take account of the observations which form the experimental basis of the theory of electrolytic dissociation. The ionisation of an aqueous electrolyte is supposed to consist in a further process of hydration whereby the fully hydrated molecule combines with an additional quantity of water to form two or more hydrated ions. The theory is in accord with the fact that the best ionising solvents are those which are themselves most highly associated, that complete ionisation is only possible in presence of a large excess of water in the case of aqueous solutions, and that the proportion of water required to produce a given degree of ionisation steadily increases as the temperature rises. Further evidence is furnished by the relative values of the ionic mobilities and the relationships existing between the fluidity of solutions and their electrical conductivity. The large mobilities of the H' and OH' ions indicate that these are either anhydrous or less hydrated than other ions. The minimum values of the molecular lowering of the freezing point which have been observed for many aqueous salt solutions between 0.1 and 0.5 normal concentrations can also be satisfactorily explained.

For a given solution the chief constants are H , the total hydration, which expresses the total number of molecules of water per molecule of solute, h , the average molecular hydration, and β , the coefficient of combination, which is the fraction of the total number of water molecules actually combined with the solute to form hydrates. These constants are connected by the equation $h = \beta H$.

On the basis of freezing-point data, the molecular hydration of aluminium chloride in solutions varying in concentration from 2.1 to 0.20 molecular has been calculated, and the values of H , h , and β are tabulated. As the concentration decreases from 2.1 to 0.2 molecules per litre, the value of h increases from 20.6 to 35.7. At greater dilutions there is an abrupt fall in the value of h , but this is attributable to experimental errors.

The hydrate theory is applicable without any substantial alteration to all cases of heterolytic conductivity in which the electrolytic properties are due to the interaction of the solute with an ionising solvent. To extend it to autolytes (fused conductors), it is necessary to assume that the mechanism of electrolysis is similar to that which obtains in solution, and that only a part of the fused salt is directly active. In this case the ions are associated with several molecules of the salt instead of with solvent molecules. Facts are cited which support the view that such complex ions are formed.

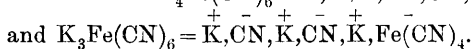
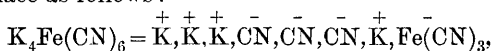
H. M. D.

Approximate Composition of the Hydrates formed by a Number of Electrolytes in Aqueous Solutions, together with a Brief General Discussion of the Results thus far obtained.

XIII. HARRY C. JONES and H. P. BASSETT (*Amer. Chem. J.*, 1905, **34**, 290—349. Compare this vol., ii, 445; *Abstr.*, 1904, ii, 386, 710, and earlier abstracts).—In continuation of the previous work, experiments have been carried out in order to obtain the data necessary for calculating the approximate composition of the hydrates formed in solutions at various concentrations. The depression of the freezing point, the conductivity at 0°, and the sp. gr. have been determined of solutions of different concentrations of lithium iodide, sodium bromide, strontium nitrate, barium iodide, cadmium nitrate, chromium chloride, potassium ferrocyanide, potassium ferricyanide, sodium chromate, sodium dichromate, disodium hydrogen phosphate, ammonium cupric chloride, potassium cupric chloride, ammonium sodium hydrogen phosphate, hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, chromic acid, sodium hydroxide, potassium hydroxide, and ammonium hydroxide. The results are tabulated and plotted as curves.

It has been shown previously that, as a rule, the number of mols. of water combined with 1 mol. of the dissolved substance increases from the most concentrated to the most dilute solution. In the case of hydrochloric, hydrobromic, nitric, and sulphuric acids, however, it is found that, starting with the more concentrated and passing to the more dilute solutions, the number of mols. of water in combination with 1 mol. of the acid passes through a maximum which is reached at a concentration of about $2N$.

From the experiments made with potassium ferrocyanide and potassium ferricyanide, it is concluded that the dissociation of these salts takes place as follows :



The following additional evidence is brought forward in favour of the theory of the existence of hydrates in solution. When a small quantity of crystallised calcium chloride or aluminium chloride is added to a fairly strong solution of cobalt chloride, the red colour of the solution is changed to blue. This change proves that calcium chloride with $6\text{H}_2\text{O}$ can, in solution, unite with a still larger quantity of water, as shown by the partial dehydration of the cobalt chloride. A similar change can be effected by the addition of salts with large hydrating power to dilute solutions of cupric bromide.

It is shown by reference to the literature that the number of mols. of water of crystallisation of a salt is greater the lower the temperature at which the salt is crystallised, and several examples are given to illustrate this fact, which, it is pointed out, affords strong evidence in support of the hydrate theory.

The paper concludes with a general discussion of all the results hitherto obtained, and a summary of the conclusions arrived at.

E. G.

Colorimetry and a Colorimetric Method for determining the Dissociation Constant of Acids. F. H. EIJDMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 166—175).—The experiments described in this paper have been carried out with a modified form of Wolff's colorimeter.

If a solution of an indicator acid (that is, an acid the anions of which have not the same colour as the acid itself) is diluted with water, the colour, as observed in the colorimeter tube, changes in the direction of the colour of the anions. If now a fairly concentrated solution of a colourless acid, HA, is gradually added until the original tint is restored in the colorimeter tube, the solution prepared from the added water and the concentrated solution of HA must be isohydric with the solution of the indicator acid. The same operation may now be repeated with another colourless acid, HA', and it is thus possible to discover the concentrations of isohydric solutions of the two acids HA and HA'. Hence, if the dissociation constant of HA is known, that of HA' may be calculated. This has been done with satisfactory results in a number of cases.

J. C. P.

Hydrolysis of Esters in Heterogeneous Systems. ROBERT KREMANN (*Zeit. Elektrochem.*, 1905, 11, 558—560).—A reply to Goldschmidt (this vol., ii, 578).

T. E.

Salt Solutions in Mixtures of Alcohol and Water. A. FLECKENSTEIN (*Chem. Centr.*, 1905, ii, 424; from *Physikal. Zeit.*, 1905, 6, 419—422).—The solubility of ammonium nitrate at different temperatures in methyl and ethyl alcohols, in water, and in aqueous alcohols was determined by dissolving known weights of the salt in the

respective solvents and reading the temperatures at which it began to be deposited from solution. In the case of ethyl alcohol, the increase of solubility is slow and is a linear function of the temperature, whereas in the case of methyl alcohol and of water the solubility increases more rapidly than the temperature. The addition of ethyl alcohol to an aqueous solution of the nitrate diminishes its solubility, whilst methyl alcohol increases it. The solubility in the mixed solvents could only be calculated at high temperatures from the law of mixtures. The formation of layers in the case of mixtures of nitrate, water, and ethyl alcohol was observed within certain limits of temperature and concentration only, and was found to depend on the amount of alcohol and not on the amount of salt. The temperature at which this separation into layers takes place varies directly as the amount of alcohol present; the phenomenon is only observed in the presence of undissolved salt. The volumes, as well as the composition, of the layers vary very much with the temperature, which is contrary to the observations of Traube and Neuberg (compare Abstr., 1888, 783) on mixtures of ammonium sulphate, water, and ethyl alcohol.

P. H.

Hydrolytic Decomposition in Non-aqueous Solutions.

GIUSEPPE BRUNI and ANTONIO MANUELLI (*Zeit. Elektrochem.*, 1905, 11, 554—555).—Formamide and acetamide are dissociated to a greater extent than water. It is therefore to be expected that they will decompose salts in an analogous way. A solution of antimony trichloride (3 grams) in formamide (5 grams) when mixed with 100 grams of the latter gives a precipitate, the composition of which lies between those of the substances $\text{SbCl}(\text{NH}\cdot\text{COH})_2$ and $\text{Sb}(\text{NH}\cdot\text{COH})_3$. When a smaller dilution is used, the composition of the precipitate corresponds with that of the first. Bismuth trichloride dissolved in formamide and antimony trichloride dissolved in acetamide behave in a similar way.

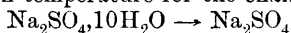
T. E.

Colloidal Solutions. CARL BENEDICKS (*Zeit. physikal. Chem.*, 1905, 52, 733—736).—The author suggests that the relation of troosite to martensite on the one hand and perlite on the other is analogous to the position of a colloidal solution intermediate between its original homogeneous solution and the resultant system of solution + precipitated substance.

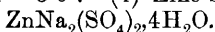
J. C. P.

Formation and Solubility of Analogous Double Salts. IVAN KOPPEL [with H. WETZEL and A. GUMPERZ] (*Zeit. physikal. Chem.*, 1905, 52, 385—436).—The author has investigated fully the conditions of existence of a series of double salts containing a common component, with the view of eliminating the influence of the accidental factors (temperature, pressure, and concentration), and detecting, if possible, those properties of the components which determine the existence and properties of the double salt. The double salts chosen for the investigation were those of the type $\text{Na}_2\text{R}''(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$, and the data sought in each case were the various transition points and the solubility at intervals up to 40° of (1) the separate components, (2) the double salt, (3) double salt + first component, (4) double salt

+ second component. Details regarding two salts of the series in question are already available, namely, for the salt $\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Roozeboom, Abstr., 1888, 1164), and for the salt $\text{CuNa}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Koppel, Abstr., 1903, ii, 78). The following other salts have been prepared, generally by mixing molecular quantities of the components at 25° or 30° ; their composition has been ascertained and the conditions of their formation studied: (1) cobalt sodium sulphate, $\text{CoNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The temperature of formation of this double salt is 17.5° ; the transition temperature for the change



is 31.5° in presence of the double salt; the cryohydric point for cobalt sulphate heptahydrate is -3.0° , but -4.5° for a mixture of the heptahydrate and sodium sulphate decahydrate. (2) Nickel sodium sulphate, $\text{NiNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The temperature of formation is 16.5° ; the sodium sulphate transition point is 31.8° in presence of the double salt. The cryohydric points for (a) nickel sulphate heptahydrate and (b) a mixture of the heptahydrate and sodium sulphate decahydrate are -3.9° and -5.1° respectively. (3) Ferrous sodium sulphate, $\text{FeNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. The temperature of formation is 18.5° ; the sodium sulphate transition point is 31.4° in presence of this double salt; the two cryohydric points corresponding with those previously mentioned are -2.0° and -3.0° . (4) Zinc sodium sulphate,



The temperature of formation is 8.7° ; the temperature of the transition $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is 37.4° in presence of the double salt; the sodium sulphate transition point is 31.5° in presence of the double salt; the cryohydric points are -6.5° and -8.3° . (5) Cadmium sodium sulphate, $\text{CdNa}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. The temperature of formation is -14.8° ; the sodium sulphate transition point is 31.0° in presence of the double salt; the two cryohydric temperatures are -16.8° and -17.7° .

It is noteworthy that the only double salts crystallising with $2\text{H}_2\text{O}$ instead of $4\text{H}_2\text{O}$ are those containing copper and cadmium, the sulphates of which crystallise with fewer than the normal seven molecules of water. The analogy of the double salts is well seen when the solubility curves for the various systems are represented graphically and compared. The temperature-coefficients of the solubilities of the different double salts are also much alike. The transition interval is small for all the double salts studied. The application of the law of mass action to a solution saturated with the two components and kept below the temperature of formation leads to the conclusion that for analogous salts, the stability range of which is reached by raising the temperature, a small solubility of the double salt, or a high solubility of the components, makes for a low temperature of formation. This conclusion is in general supported by the experimental evidence. J. C. P.

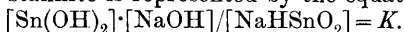
Use of the Differential Equation in Calculating the Results of Kinetic Measurements; the Reaction between Arsenic Acid and Potassium Iodide near the Equilibrium. W. C. BRAY (*J. Physical Chem.*, 1905, 9, 573—587).—In certain cases in which the rate of a reaction is being investigated, the integrated expression may be so complicated that it is difficult to obtain values for the constants,

The author indicates a method by the use of the differential equation itself. A preliminary constant is first calculated from as simple an equation as possible, and from this the final constant is obtained from the differential equation. In these cases the values dx/dt must be taken from a curve representing x against t . The applicability of the method of investigation is proved by applying it to the results obtained by Roebuck for the reaction between arsenic acid and potassium iodide (Abstr., 1903, ii, 14), and the final result of the recalculations is that there is better agreement with the theory than was claimed in the original paper.

L. M. J.

Kinetic Study of Organic Reactions. HEINRICH GOLDSCHMIDT (*Chem. Centr.*, 1905, ii, 749—750; from *Naturw. Rundsch.*, 1905, 20, 365—368).—The reduction of the three nitrophenols, nitroanilines, nitrobenzoic acids, and nitrobenzenesulphonic acids, and of *o*-nitrobenzaldehyde in alkaline tin solutions has been studied.

The equilibrium between stannous hydroxide, sodium hydroxide, and monosodium stannite is represented by the equation



When stannous hydroxide is present as a solid phase, its concentration is constant, and experiments under these conditions show that the ratio $[\text{NaOH}] / [\text{NaHSnO}_2]$ is constant = 2.2 over a large concentration interval. The solubility of stannous hydroxide is 0.000014 mol. per litre, from which it is calculated that the hydrolytic constant of monosodium stannite has the value 0.00003, and the affinity constant of stannous hydroxide, regarded as a monobasic acid, the value $4 \cdot 10^{-10}$. If the solution is acted on by free oxygen, the concentration of the sodium hydroxide is diminished in consequence of the formation of sodium stannate.

The velocity of reduction when the concentration of the nitro-compound and of the stannous hydroxide is very small and the concentration of the alkali is constant is given by the equation $v = k \cdot C_{\text{NO}_2} \cdot C_{\text{Sn}}$. It would appear, however, that two reducing substances are present in the alkaline solution, one of which is supposed to be the ion HSnO_2^- , the other undissociated NaHSnO_2 , and the general expression for the rate of reduction is $v = k \cdot C_{\text{NO}_2} \cdot C_{\text{HSnO}_2^-} + k' C_{\text{NO}_2} \cdot C_{\text{NaHSnO}_2} \cdot C_{\text{OH}^-}$. The factor C_{OH^-} in the second term expresses the fact that the influence of the sodium hydroxide is greater than that which corresponds simply with a diminution of the dissociation of the sodium salt.

On reduction of *o*- and *p*-nitrophenols, *o*- and *p*-nitroanilines pass directly into the amines; the corresponding meta-compounds and the other nitro-compounds examined give rise to mixtures of azo- and azoxy-compounds. *o*-Nitrobenzoic acid is an exception and forms a hydroxylamine derivative.

The mechanism of the process is represented by the equations (1) $\text{RNO}_2 - \text{O} = \text{RNO}$, (2) $\text{RNO} - \text{O} = \text{RN}=\text{}$, (3) $2\text{RN}=\text{RN}=\text{NR}$, or $\text{RN}=\text{} + \text{H}_2\text{O} = \text{RNH} \cdot \text{OH}$.

The rate of reduction of the nitro-compounds by stannous chloride in hydrochloric acid solution is expressed by the equation

$$v = k \cdot C_{\text{NO}_2} \cdot C_{\text{SnCl}_2} \cdot C_{\text{HCl}}.$$

Replacement of the hydrochloric acid by sodium chloride produces no alteration in the velocity, and the author concludes that the process is a reaction in which complex halogen ions, SnCl_3' , act the part of a catalyst. Addition of potassium iodide has a similar effect, and the reduction by stannous bromide is accelerated by the addition of potassium bromide. The author's view of the reduction agrees with that of Haber and is expressed by the equations (1) $\text{R}\cdot\text{NO}_2 + 2\text{H} = \text{R}\cdot\text{NO} + \text{H}_2\text{O}$, (2) $\text{R}\cdot\text{NO} + 2\text{H} = \text{R}\cdot\text{NH}\cdot\text{OH}$, (3) $\text{R}\cdot\text{NH}\cdot\text{OH} + 2\text{H} = \text{R}\cdot\text{NH}_2 + \text{H}_2\text{O}$, the first and third reactions taking place with finite, the second with infinitely great velocity. H. M. D.

Oxidation and Reduction. NICOLAAS SCHOORL (*Rec. Trav. chim.*, 1905, [ii], 24, 327—330).—A theoretical paper. M. A. W.

Mechanism of the Beckmann Intramolecular Transformation. C. H. SLUITER (*Rec. Trav. chim.*, 1905, [ii], 24, 372—376).—An account of work already published (compare Lobry de Bruyn and Sluiter, *Abstr.*, 1904, ii, 473). M. A. W.

A New Case of Catalysis by Hydrogen Ions. GEORG BREDIG and W. FRAENKEL (*Zeit. Elektrochem.*, 1905, 11, 525—528).—The velocity of hydrolysis of ethyl diazoacetate into nitrogen and ethyl glycolate in presence of hydrogen ions is shown to be strictly proportional to the concentration of the undecomposed ester (at constant temperature), and also very nearly proportional to the concentration of the hydrogen ions calculated from the conductivity. The following average values are given for the ratio of velocity constant and concentration of hydrogen ions: nitric and picric acids 34.9, acetic, succinic, and benzoic acids 32.5. The reaction takes place rapidly in presence of very small quantities of hydrogen ions (in presence of $1/2000$ *N*-nitric acid at 25° , it is half finished in $\frac{3}{4}$ hour); it is, therefore, very well suited for the estimation of very small concentrations of hydrogen ions. T. E.

Heterogeneous Catalytic Reactions. III. Catalytic Influence of Silica on the Reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$. MAX BODENSTEIN and FRIEDRICH OHLMER (*Zeit. physikal. Chem.*, 1905, 53, 166—176. Compare Kühl, *Abstr.*, 1903, ii, 639).—The reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ is catalytically accelerated when it takes place in a vessel of quartz-glass. The rate of the change is adequately represented by the empirical formula $dx/dt = k(m + a - x)/(n + b - x)$, where a and b are the initial concentrations of oxygen and carbon monoxide respectively, m and n are constants. The chief feature of the investigation is the fact that carbon monoxide retards its own combustion in the quartz-glass vessel, so that the velocity of the reaction is almost inversely proportional to the concentration of carbon monoxide. This, therefore, is to be regarded as a case of negative autocatalysis. This peculiarity is not observed when the reaction takes place in an ordinary glass vessel containing pieces of quartzite or rock crystal. With both these catalysts, the reaction velocity is directly proportional to the carbon

monoxide concentration, and proportional also, although only roughly, to the square root of the oxygen concentration.

In all cases, the temperature-coefficient (for an interval of 10°) was between 1.4 and 1.8. J. C. P.

Catalysis by Ferments. HANS EULER (*Zeit. physiol. Chem.*, 1905, 45, 420—447. Compare this vol., ii, 378).—A review is given of the physico-chemical measurements hitherto made relating to ferment action. The influence of substrate and ferment concentration on the reaction formula is given in tabular form. These fall into certain systems.

The exceptions noted in the simple reaction laws have been attributed by most authors to an intermediary union between the ferment and the substrate; although this is not entirely satisfactory, it is at present the best available explanation. The methods of action of ferments and inorganic catalytic agents proceed on similar lines. Both increase the concentration of the active molecules. W. D. H.

Experimental Demonstration of the Indestructibility of Matter and of the Law of Multiple Proportions. Structure of the Bunsen Flame. Two Alloys. JOSEPH HABERMANN (*Chem. Centr.*, 1905, ii, 379; from *Verh. naturf. Ver. Brinn.*, 1905, 43).—It may be shown that a closed 250 c.c. flask filled with hydrogen and containing 0.5 gram of finely-powdered copper oxide undergoes no change in weight if gently heated until the oxide is reduced to metallic copper.

Sodium hydrogen carbonate reacts with barium chloride as follows: (i) $2\text{NaHCO}_3 + \text{BaCl}_2 = 2\text{NaCl} + \text{BaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$; the addition of hydrochloric acid to this mixture produces the evolution of a further quantity of carbon dioxide (ii) $\text{BaCO}_3 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$, equal in volume to that produced according to equation (i). The law may be demonstrated by collecting the two volumes successively in an apparatus specially adapted for the purpose.

A modification of the experiments of Teclu (compare Abstr., 1891, 1309) and Haber and Richardt (Abstr., 1904, ii, 166) is devised to show the structure of the Bunsen flame.

The small amount of iron found in two samples of alloys of copper, zinc, and iron which had been used in covering a roof is attributed to the removal of this metal by atmospheric agency. P. H.

The Condition which determines the Chemical Similarity of Elements and Radicles. GEOFFREY MARTIN (*J. Physical Chem.*, 1905, 9, 562—572).—If the ratios of the heats of combination of chlorine and bromine with metals be compared, it will be found that the ratios are almost independent of the combining metal. Thus in the case of fifteen metals investigated, the ratios only vary between 1.11 and 1.34. In the case of elements such as iodine and oxygen, the ratios vary greatly, for example (excluding negative signs), 0.21 to 3.78. This constancy of ratio the author considers to be the condition of similarity, and is exemplified by the cases of fluorine and chlorine,

sodium and potassium, potassium and caesium, zinc and cadmium, boron and silicon, calcium and strontium, strontium and barium, nickel and cobalt, antimony and bismuth.

L. M. J.

Dewar's Method of Producing High Vacua. LORD BLYTHSWOOD and H. S. ALLEN (*Phil. Mag.*, 1905, [vi], 10, 497—512. Compare Dewar, *Proc. Roy. Soc.*, 1904, 74, 122, and Abstr., 1904, ii, 652).—Dewar's method is applicable in the exhaustion of large receivers, and only a moderate amount of liquid air is required. The amount of air absorbed by a given quantity of charcoal at the temperature of liquid air is nearly independent of the pressure. The rate of absorption at any moment is proportional to the difference between the total amount of air that can be absorbed and the amount already absorbed.

J. C. P.

Lecture Experiments. ROBERTO SALVADORI (*Gazzetta*, 1905, 35, ii, 27—28).—The apparatus employed by the author to demonstrate the law of conservation of weight during chemical reactions and the laws of combination of gases by volume consists of a glass tube divided by means of three stopcocks into two parts of equal capacity. One of these parts can be filled, for example, with ammonia and the other with hydrogen chloride, and it can then be shown that no change in weight accompanies the reaction taking place on opening the middle cock. The method of using the apparatus to show the combination of different gases in equal or multiple volumes is obvious

T. H. P.

Lecture Experiment for the Demonstration of Solid Solutions. ERNST BECKMANN (*Zeit. physikal. Chem.*, 1905, 53, 151—152).—As was shown some time ago by the author, solutions of iodine in *p*-xylene deposit the pure solvent on freezing, whilst from solutions of iodine in benzene a solid solution is obtained on freezing. If solutions of iodine in these two solvents are partially frozen, and the crystals separated from the mother liquors in a suitable centrifugal machine, the difference is at once apparent.

J. C. P.

New Laboratory Apparatus. OTTORINO ANGELUCCI (*Gazzetta*, 1905, 35, ii, 142—144).—The author describes: (1) an automatic apparatus for washing precipitates and (2) a constant-level feeding siphon, by means of which it is possible to keep water circulating in a vessel and to maintain the level of the water at a constant height.

T. H. P.

Inorganic Chemistry.

Reducing Action of Hydrogen. ALFRED C. CHAPMAN and H. D. LAW (*Analyst*, 1905, 30, 306—307).—In the case of dilute sulphuric acid and zinc, hydrogen is only liberated when the solution tension of the metal is greater than that of hydrogen, which is about 1 volt, whilst the solution tension of zinc is about 1·7 volts. Every metal, however, exerts a retaining effect on the hydrogen formed at its surface, so that a potential far in excess of that of the hydrogen electrode is necessary before any free hydrogen is liberated. This excess of potential is known as supertension. Metals, such as palladium, platinum, copper, nickel, cobalt, silver, and iron, having low supertensions, when deposited on the surface of pure zinc increase the rate at which the hydrogen is liberated, but reduce its activity to such an extent that it is incapable of reducing such substances as arsenic oxide, &c. Cadmium, lead, and tin, which have high supertensions, have no effect on the reducing power of the zinc. These considerations explain the insensitiveness of some samples of zinc in the Marsh-Berzelius test.

W. P. S.

Union of Hydrogen with Oxygen at Low Pressures caused by the Heating of Platinum. P. J. KIRKBY (*Phil. Mag.*, 1905, [vi], 10, 467—476).—Platinum in the presence of hydrogen and oxygen at a low pressure does not cause these gases to combine perceptibly, unless its temperature exceeds a certain critical value. This value is nearly independent of the pressure of the mixed gases (at least for pressures between 2 and 40 mm. mercury) and lies at about 275° for pure platinum; for impure platinum, this critical temperature appears to be lower. When the combination of the gases has once been started by heating the platinum sufficiently, the reaction may be temporarily renewed by raising the platinum to a temperature distinctly lower than that required to start the reaction. The reaction between the gases is not produced by the mere heating to a temperature at which they combine spontaneously, but probably is connected with the corpuscular discharge which is known to be emitted by platinum.

J. C. P.

Cause of the Green Tint of Natural Waters. WALTÈRE SPRING (*Arch. Sci. phys. nat.*, 1905, [iv], 20, 101—110).—The colour of pure water is blue, the green and yellow tints of natural waters are due to foreign admixture. Calcium salts dissolved in water seem to give a green tint, but the author shows that this is due to a fine invisible suspension (probably organic matter and silica) and that with adequate precautions calcium salts have no effect on the colour of water. The brown or yellow colours are due to humus or salts of iron; both these are precipitated, however, if calcium salts are present. The latter, therefore, assist in restoring the natural colour of water and the green tint is often due to a state of stationary equilibrium

between the precipitating effect of the calcium salts and the continuous admixture of humus or ferric salts. L. M. J.

Some Properties of the Hydrides of the Metalloids of the First Three Families. ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1905, [viii], 5, 289—307. Compare Abstr., 1902, ii, 253, 254, 379, 498, 557; this vol., ii, 310, 372).—The correlation of boiling point, melting point, heat of formation, and specific gravity in the liquid state with the molecular weight of each of the members of these three groups of hydrides is studied and in part exhibited by means of curves. It is shown that in general the difference between the values of any one of these constants for two consecutive hydrides of the same group is proportional to the difference between the molecular weights of the two hydrides and that in each series the volatility and fusibility diminish and the specific gravity and heat of formation increase as the molecular weight augments.

The hydrides of the first members and, to a less extent, those of the last members, of each group show abnormalities. It is pointed out that in the case of the former the abnormality may be due to association, but this explanation does not account for all the facts, and it is more probably due to the peculiar chemical constitution of these hydrides. Observations are already on record of other abnormalities in the behaviour of water, hydrofluoric acid, and ammonia, the three hydrides in question. T. A. H.

The Castner Mercury Process of obtaining Chlorine and Alkali. MAX LE BLANC and CARLO CANTONI (*Zeit. Elektrochem.*, 1905, 11, 609—612).—A description of a laboratory model of the Castner electrolytic cell. Experiments with the model are described in which potassium hydroxide is prepared from potassium chloride with a current efficiency of 90 per cent. T. E.

Atomic Weight of Chlorine. HAROLD B. DIXON and E. C. EDGAR (*Phil. Trans.*, 1905, A, 205, 169—200).—The method adopted, as outlined by the authors, was as follows. Chlorine obtained by electrolysis of fused silver chloride (with purified carbon poles in a Jena glass vessel) was condensed and weighed in a sealed glass bulb; this bulb was attached to an exhausted "combustion globe," and the chlorine was allowed to evaporate slowly into the globe. The hydrogen, prepared by the electrolysis of barium hydroxide, was dried and absorbed by palladium in a weighed vessel. The palladium, on being heated, gave off the hydrogen, which was ignited by a spark and burnt at a jet in the combustion globe previously filled with chlorine. The gases were regulated so as to maintain the hydrogen flame until nearly all the chlorine had combined; then the palladium was allowed to cool, and the hydrogen was turned off just before the flame died out. The hydrogen chloride formed was dissolved by water standing in the globe, which was kept cool with ice. The residual gas in the globe was analysed, and the chlorine remaining in the globe unburnt was determined by breaking a thin glass bulb containing potassium iodide and titrating the liberated iodine by thiosulphate in an atmosphere of

carbon dioxide. In each experiment, about 11 litres each of hydrogen and chlorine were burnt; the volume of chlorine left unburnt was about 2 per cent. of the volume burnt. The chlorine and hydrogen bulbs were counterpoised on the balance by bulbs of the same glass and of nearly the same displacement, and the small weights used were reduced to a vacuum standard. Nine experiments were made, and the mean value obtained for the atomic weight of chlorine is 35.463 ($O=16$), appreciably higher than the value 35.447 calculated by Clarke from the previous determinations, and slightly higher than Stas' value, 35.457.

Incidentally, it was shown that neither gaseous nor liquid chlorine has any appreciable effect on soft glass. J. C. P.

Chlorine. DAVID L. CHAPMAN and CHARLES H. BURGESS (*Mem. Manchester Phil. Soc.*, 1905, 49, xiii, 1—3. Compare this vol., ii, 236).—Small quantities of ether, alcohol, and benzene have no effect on the combination of hydrogen and chlorine; they do not give rise to an induction period. Experiments carried out to ascertain which possible chemical compound is immediately active in the induction period caused by the presence of traces of ammonia indicate that this is nitrogen chloride. When the gaseous mixture is exposed to light until the rate of combination is a maximum and is then left for some time in the dark, a second induction period occurs on exposure to light if the water contains traces of organic matter. This is probably due to the action of chlorine on the organic substances in the dark, with the formation of compounds which then prevent the combination of hydrogen and chlorine in the light. The opinion expressed previously that sulphur dioxide behaves similarly to ammonia is not confirmed by further experiments. H. M. D.

Electrolytic Formation of Chlorates. FRITZ FOERSTER and ERICH MÜLLER (*Zeit. Elektrochem.*, 1905, 11, 502—503).—The acceleration of the reaction between hypochlorous acid and hypochlorite ion by platinum studied by Sirk (this vol., ii, 381) was observed by the authors previously (*Abstr.*, 1902, ii, 591 and 641). They showed it to be of secondary importance in the formation of chlorates. T. E.

Theory of Auto-oxidation. JULIUS MEYER (*J. pr. Chem.*, 1905, [ii], 72, 278—296).—The theories of the mechanism of auto-oxidation held by various authors are reviewed. The one which agrees best with the experimental facts is that auto-oxidation consists of the addition to an unsaturated molecule of a molecule of oxygen, one atom of which functions as quadrivalent. The grouping $O:O:$ is probably more common and more stable than the union of two quadrivalent oxygen atoms, as amongst the nitrogen compounds the grouping $N''':N'$ is more common and more stable than the union of two quinquivalent nitrogen atoms. According to this view, hydrogen peroxide, which exists in the unimolecular state only, has the constitution $O:OH_2$, whilst water exists in the bimolecular, $OH_2:OH_2$, as well as in the unimolecular form (compare Brühl, *Abstr.*, 1896, ii, 163). The peroxides must have corresponding formulæ, for example,

ozone, $O\cdot O\cdot O$; barium oxide, $O\cdot O\cdot Ba$; potassium dioxide, $O\cdot O\cdot K_2$; and sodium hydrogen peroxide, $O\cdot OHNa$ (Tafel, Abstr., 1894, ii, 448).

The several reactions of hydrogen peroxide and of its derivatives are explained by means of, and shown to be in agreement with, the suggested constitutions.

As hydrogen peroxide acts principally as a reducing agent, giving up hydrogen and forming oxygen, the bivalent oxygen atom must be more firmly united to the quadrivalent atom than are the hydrogen atoms.

G. Y.

Electrical Production of Ozone. OSCAR KAUSCH (*Chem. Centr.*, 1905, ii, 438; from *Elektrochem. Zeit.*, 1905, 12, 69—74).—An account of the various forms of apparatus devised by Strong, Courtis, Jarnold, and Otto for the preparation of ozone.

P. H.

Action of Alkali [Hydroxides] on Sulphur. H. POMERANZ (*Zeit. Farb. Text. Ind.*, 1905, 4, 392—393).—The author supposes that the primary action between alkali hydroxides and sulphur is analogous to that between alkali hydroxides and chlorine in the cold, and takes place according to the equation $4NaOH + 2S = Na_2S + Na_2SO_2 + 2H_2O$ or $3NaOH + 2S = Na_2S + NaHSO_2 + H_2O$. In support of this view, it is found that a mixture of sulphur and sodium hydroxide in the ratio $2S : 3NaOH$ has a similar bleaching action on *p*-nitro-aniline-red to that of sodium hyposulphite. Polysulphide and thio-sulphate are only produced by the further action of the sulphur on the sulphide and hyposulphite. The formula H_2SO_2 for the hyposulphites harmonises with the author's observations, but Bernthsen's formula is inadmissible.

H. M. D.

Polysulphides. III. Periodic Phenomena during the Electrolysis of Polysulphides. FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1905, 46, 113—143).—If a fairly concentrated solution of disodium sulphide is electrolysed between platinum electrodes with an *E.M.F.* of about 2 volts, yellow films due to the formation of polysulphide separate out in the liquid. After a time, sulphur suddenly appears on the surface of the anode, and then rapidly increases in thickness. The *E.M.F.* rises as the thickness of the sulphur increases, until at a certain stage the sulphur film suddenly breaks away; the *E.M.F.* now falls, and the phenomena recur in the same order. This periodicity is similar to that observed by Ostwald during the solution of chromium in hydrochloric acid (Abstr., 1900, ii, 730; 1901, ii, 24), and has been studied quantitatively by means of a modified Ostwald chemograph.

[With K. KOELICHEN.]—The form of the curves which express the periodicity of current strength is very varied.

Apart from the condition of the anode and electrolyte, it is found that the *E.M.F.*, and consequently the current strength, must have a certain magnitude before sulphur separates and the periodicity appears. On the other hand, the *E.M.F.* must not be too great or the deposit of sulphur remains permanently on the anode. The "critical

E.M.F." depends on the chemical composition of the electrolyte, its concentration, temperature, and its stillness or otherwise. In solutions of sodium hydrosulphide, no periodic phenomena are observed. In disodium sulphide solutions, the periods begin after about 7 to 8 per cent. of the sulphide has been converted into polysulphide. If the ratio of polysulphide to sulphide in the solution exceeds a certain limit, the fluctuations no longer occur. Increasing concentration of sulphide or rising temperature causes increasing complication in the form of the periodicity curve. The higher the temperature, the greater the current density needed to cause vibrations to appear; the amplitude of the vibrations and the critical *E.M.F.* increase at first with rising temperature and then fall. The form of the curves is largely dependent on the form and surface of the electrodes.

It is suggested that during electrolysis the sulphur liberated at first at the anode is taken up by the sulphur ions of the solution to form polysulphide ions until saturation occurs; sulphur then separates, and the current becomes feeble owing to the resistance of the sulphur. During the time when the current is feeble, the polysulphide ions migrate away from the anode more quickly than they are formed, whilst the monosulphide ions (which can take up sulphur) migrate towards the anode and eventually break down the layer of sulphur.

D. H. J.

Constitution of Fremy's Sulphazilate and of Pelouze's Nitrosulphate. ARTHUR HANTZSCH (*Ber.*, 1905, 38, 3079—3082).—A reply to Divers, this vol., ii, 449. J. J. S.

Sulphammonium and its Relation to Nitrogen Sulphide. OTTO RUFF and EMIL GEISEL (*Ber.*, 1905, 38, 2659—2667. Compare Abstr., 1904, ii, 396; Moissan, Abstr., 1901, ii, 234).—Hydrogen sulphide and nitrogen sulphide are formed by the action of sulphur on liquid ammonia according to the equation $10S + 4NH_3 = 6H_2S + N_4S_4$. The hydrogen sulphide is completely precipitated as silver sulphide, and the blue colour of the sulphammonium is changed into the orange-red of a solution of nitrogen sulphide in ammonia when silver iodide (12 mols.) is added to sulphur (10 atoms) dissolved in liquid ammonia. The nitrogen sulphide is isolated by evaporating the filtrate, heating the residue at 100° for two hours, and extracting with carbon disulphide. If a current of air is passed through sulphammonium as soon as the liquid ammonia is evaporated, ammonium sulphide volatilises and is detected by means of lead nitrate; the residue contains sulphur and nitrogen sulphide. The reaction is reversible, as, if hydrogen sulphide is condensed over a solution of nitrogen sulphide in ammonia cooled by liquid air in a tube which is sealed and allowed to assume slowly the ordinary temperature, a blue ring is formed at the junction of the two liquids, which rapidly disappears as the hydrogen sulphide is absorbed. On evaporating the ammonia, a residue is obtained consisting of sulphur together with the excess of ammonium sulphide. Sulphammonium is formed also by the action of hydrogen sulphide on nitrogen sulphide in ammonia at -35°

or of ammonia and a limited amount of hydrogen sulphide on lead or mercury dithiodi-imide.

The blue colour of sulphammonium is due most probably to dissolved colloidal sulphur.

G. Y.

Theory of the Lead Chamber Process. III—V. FRITZ RASCHIG (*Zeit. angew. Chem.*, 1905, 18, 1281—1323. Compare this vol., ii, 23).—A lecture delivered to a joint meeting of the Oberrheinischer Bezirksverein deutscher Chemiker and the Heidelberg Chemischen Gesellschaft. The theory of the lead chamber process is dealt with in great detail and the following conclusions are drawn. Nitric oxide quickly combines with oxygen to form nitrogen trioxide, which then undergoes slow oxidation to form nitric peroxide. In the atmosphere of the lead chamber, nitric oxide is oxidised to nitrous acid in about three seconds; the further oxidation to the peroxide requires about five minutes for its completion. The particular oxide of nitrogen which in the lead chamber combines with sulphurous acid is the trioxide, a conclusion which is also borne out by the behaviour of nitric peroxide and nitrogen trioxide respectively towards sulphur dioxide in the presence of water; nitric peroxide dissolves in water to form a mixture of nitric and nitrous acids, whilst only the latter acid unites with sulphur dioxide. Nitrogen trioxide, on the other hand, unites directly with sulphurous acid. Nitrogen trioxide is readily soluble in concentrated sulphuric acid; it is not so readily soluble either in aqueous sodium hydroxide or in water. When nitrogen trioxide is dissolved in water, it is partially decomposed into nitric oxide and nitric peroxide, the former being eliminated as a gas and the latter dissolving to form a mixture of nitrite and nitrate. On the other hand, nitric peroxide is readily soluble in aqueous sodium hydroxide to form a mixture of nitrite and nitrate; it is soluble with difficulty in sulphuric acid, when it undergoes decomposition with the evolution of some oxygen.

The compound obtained by dissolving nitrogen trioxide in sulphuric acid is not a nitrosylsulphuric acid, $\text{O:N}\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$, as is generally assumed, but is a nitrosulphonic acid, $\text{O}_2\text{N}\cdot\text{SO}_2\cdot\text{OH}$, the sulphur atom being attached directly to the nitrogen atom. When this compound is reduced, the acid $\text{O:N(OH)}\cdot\text{SO}_2\cdot\text{OH}$ is produced. The latter acid forms a blue solution with concentrated sulphuric acid; with more dilute sulphuric acid, it forms a red coloration, which becomes violet when copper sulphate is added; it is very unstable, the products of its decomposition being nitric oxide and sulphuric acid. With copper and iron respectively, it forms compounds of the nature of salts, the solutions of which in concentrated sulphuric acid do not give off nitric oxide on being agitated.

In the Glover tower, nitrous acid is first formed from nitrosulphonic acid; nitroso- and nitroso-sulphonic acids are next formed, and finally nitric oxide and sulphuric acid. Nitric oxide is further oxidised to nitrous acid, which combines with sulphurous acid to form nitric oxide and sulphuric acid.

The process in the lead chamber is represented by the equations: (1) $\text{NO}\cdot\text{OH} + \text{SO}_2 = \text{NO}\cdot\text{SO}_2\cdot\text{OH}$, (2) $\text{NO}\cdot\text{SO}_2\cdot\text{OH} + \text{NO}\cdot\text{OH} = \text{NO} +$

$\text{NO}(\text{OH})\cdot\text{SO}_2\cdot\text{OH}$, (3) $\text{NO}(\text{OH})\cdot\text{SO}_2\cdot\text{OH} = \text{NO} + \text{H}_2\text{SO}_4$, (4) $2\text{NO} + \text{O} + \text{H}_2\text{O} = 2\text{NO}\cdot\text{OH}$.
A. McK.

The Contact Process of Manufacturing Sulphuric Acid. RICHARD LUCAS (*Zeit. Elektrochem.*, 1905, 11, 457—461).—Bodländer and Köppen (Abstr., 1903, ii, 639) studied the equilibrium between sulphur dioxide and oxygen by the manometric method; the author (this vol., ii, 396), having found that pure platinum does not absorb oxygen, has completed the work by making measurements at temperatures above 600° . His results are summarised in the following table, in which $K = [\text{SO}_2]^2[\text{O}_2]/[\text{SO}_3]^2$.

Temperature.	K .
500°	0.1646×10^{-5}
600	0.2720×10^{-4}
700	0.2525×10^{-3}
800	0.1548×10^{-2}

T. E.

Colloidalising Action of Caoutchouc on Selenium. RUDOLF DITMAR (*Chem. Centr.*, 1905, ii, 741; from *Sitzungsber. Akad. Wiss. Wien*, 1905).—When a solution of isinglass to which a few drops of gold chloride solution have been added is warmed, a blood-red coloration makes its appearance. On addition of a larger quantity of gold chloride, the solution assumes a violet and then a black colour. When finely-divided metallic gold is used instead of the chloride, the gold does not assume the colloidal form. On the other hand, caoutchouc mixed and warmed with finely-divided black, amorphous selenium assumes the dark red colour of colloidal selenium. This is the first observed case of the direct transmission of the colloidal condition to an element under the contact influence of a colloid. The observation supports the view that the sulphur in vulcanised caoutchouc is present in the colloidal form. Attempts to vulcanise caoutchouc with selenium were unsuccessful.
H. M. D.

Chemistry of the Tellurates. EDGAR BURTON HUTCHINS, jun. (*J. Amer. Chem. Soc.*, 1905, 27, 1157—1183).—When silver oxide is treated with slight excess of a solution of telluric acid, silver tellurate, $\text{Ag}_2\text{TeO}_4\cdot 2\text{H}_2\text{O}$, is obtained as a heavy, granular powder which differs in physical properties from the compound described by Berzelius (*Ann. Phys. Chem.*, 1834, [ii], 32, 577). This salt can be obtained in a crystalline form by the slow evaporation of a mixture of silver acetate and telluric acid solutions or by the action of silver nitrate on a concentrated solution of potassium tellurate containing a little free acetic acid. The crystals belong to the orthorhombic system [$a:b:c = 0.722:1:2.107$]. When this salt is left in contact with a solution of a silver salt, the basic tellurate, $3\text{Ag}_2\text{O}\cdot 2\text{TeO}_3\cdot 3\text{H}_2\text{O}$, is obtained in the form of red crystals.

The crystalline compound described by Oppenheim (*J. pr. Chem.*, 1857, 71, 266) as a double salt of silver nitrate and tellurate is the

salt $\text{Ag}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$. The acid tellurates of silver described by Berzelius (*loc. cit.*) could not be obtained. In addition to the basic tellurates of silver, $3\text{Ag}_2\text{O} \cdot 2\text{TeO}_3$ and $3\text{Ag}_2\text{O} \cdot \text{TeO}_3$, described by Berzelius, another compound, $3\text{Ag}_2\text{O} \cdot 2\text{TeO}_3 \cdot 3\text{H}_2\text{O}$, has been isolated, which crystallises in red, transparent, monoclinic prisms.

Crystalline potassium tellurate, $\text{K}_2\text{TeO}_4 \cdot 5\text{H}_2\text{O}$, cannot be obtained by treating potassium carbonate with telluric acid, as stated by Berzelius (*loc. cit.*), since telluric acid is unable to replace the whole of the carbonic acid in an equivalent quantity of potassium carbonate. The crystals can, however, be obtained by the slow evaporation of a solution of the salt prepared from potassium hydroxide and telluric acid or of the solution formed by the interaction of silver tellurate and potassium bromide. The existence of the salt $\text{K}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, described by Retgers (Abstr., 1893, ii, 161), is confirmed. The acid potassium tellurates, KHTeO_4 and $\text{K}_2\text{O} \cdot 4\text{TeO}_5$, described by Berzelius (*loc. cit.*), crystallise as $\text{K}_2\text{O} \cdot 2\text{TeO}_3 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{O} \cdot 4\text{TeO}_3 \cdot 4\text{H}_2\text{O}$ respectively. When a solution of potassium carbonate (1 mol.) is added to a solution of telluric acid (4 mols.) and the mixture is evaporated, the salt $\text{K}_2\text{O} \cdot 3\text{TeO}_3 \cdot 5\text{H}_2\text{O}$ is obtained as a white, granular precipitate.

When mercurous tellurate (Berzelius, *loc. cit.*) or mercurous nitrate is treated with a cold concentrated solution of telluric acid, *mercurous hydrogen tellurate*, $\text{HgHTeO}_4 \cdot 3\text{H}_2\text{O}$, is obtained, which forms triclinic crystals. Two *mercuric tellurates*, Hg_3TeO_6 and $\text{HgTeO}_4 \cdot 2\text{H}_2\text{O}$, have been prepared; the former is obtained in amber-coloured crystals of the cubic system, whilst the latter is white and crystallises in the rhombic system; an amorphous *mercuric tellurate*, HgTeO_4 , is described, which is obtained as a light yellow powder.

The compound obtained by the action of potassium tellurate on copper nitrate is not copper tellurate, CuTeO_4 , as stated by Berzelius, but is the *orthotellurate*, Cu_3TeO_6 . The corresponding zinc salt, Zn_3TeO_6 , is also described. Attempts were made to prepare a gold tellurate, but without success.

Hot concentrated solutions of telluric acid attack mercury, silver, lead, tin, arsenic, antimony, bismuth, nickel, zinc, aluminium, and cadmium.

There are no well authenticated cases of isomorphism between sulphates and tellurates or between selenates and tellurates. E. G.

Determination of the Atomic Weight of Nitrogen; Gravimetric Analysis of Nitrous Oxide. PHILIPPE A. GUYE and STEFAN BOGDAN (*J. Chim. Phys.*, 1905, 3, 537—561).—A more detailed account of work already published (Abstr., 1904, ii, 575; see also Abstr., 1904, ii, 475, 812; this vol., ii, 506). L. M. J.

Preparation of Oxides of Nitrogen by High Tension Discharges in Air. OTTO SCHEUER (*Zeit. Elektrochem.*, 1905, 11, 565—580).—An arc discharge between metal poles is used, the current being furnished either by a Ruhmkorff coil or by a step-up transformer. A large number of different forms of electrode is described. The general results are that in order to obtain good yields the air must

pass through the flame and be at once cooled and removed; the shape, size, and arrangement of the apparatus is of the greatest importance. The kind of current used (pressure, strength of current, and frequency) is important; a large current is unfavourable. The material of the electrodes is of little importance. Ammonia is formed in addition to the oxides of nitrogen when moist air is employed. T. E.

Electrolytic Preparation of Nitrite from Nitrate, especially at Silver Cathodes. ERICH MÜLLER and FRITZ SPITZER (*Zeit. Elektrochem.*, 1905, 11, 509—515).—In continuation of the experiments of Müller and Weber (*Abstr.*, 1904, ii, 116) it is shown that cathodes of silver behave in very much the same way as those of copper. The difference between the potentials of cathodes of spongy silver in solutions of alkali nitrate and nitrite is, however, much greater than is the case with copper, and it is therefore possible by means of a silver cathode to reduce the nitrate to nitrite much more completely before any considerable formation of ammonia takes place. Gold is quite unsuitable, the potential of a gold cathode being almost the same in a solution of nitrate as in a solution of nitrite. T. E.

Phosphorus Pentasulphide. ALFRED STOCK and KURT THIEL (*Ber.*, 1905, 38, 2719—2730).—Phosphorus pentasulphide, prepared by heating at 120—130° for 12 hours a solution of yellow phosphorus and sulphur in carbon disulphide containing a trace of iodine, has the appearance of flowers of sulphur and melts at 275—276°. Phosphorus pentasulphide exists in at least two modifications; the ordinary form has the melting point quoted and differs from the others in its more sparing solubility in carbon disulphide. The two forms cannot be separated by fractional crystallisation from carbon disulphide. The form which is more readily soluble in carbon disulphide does not exhibit a sharp melting point. Ebullioscopic determinations of the molecular weight of the ordinary form in carbon disulphide shows it to have the formula P_4S_{10} . When similar determinations are made with the form which is more readily soluble in carbon disulphide, the values do not agree with the formula P_4S_{10} , the molecular weight being smaller than that in accordance with this formula; the product is probably a mixture. A. McK.

Constituents of Manchester Soot. EDMUND KNECHT (*Mem. Manchester Phil. Soc.*, 1905, 49, xiv, 1—10).—All the samples examined showed a strongly acid reaction due to presence of free sulphuric acid, which amounted to about 1 per cent. on the average. The methods of examination consisted in extracting with water, boiling dilute sulphuric acid, sodium hydroxide, and with benzene. The amounts of constituents estimated directly are:

Ammonium sulphate	10·7 per cent.
Mineral matter (ash).....	19·6 ,,
Acid constituents	10·9 ,,
Benzene extract (hydrocarbons)	13·0 ,,
Difference (carbon ?).....	45·8 ,,

A sample of London soot was found to contain considerably less extractive matter, the benzene extract only amounting to 1.3 per cent. A sample from Prague, produced by the incomplete combustion of lignite coal, gave an aqueous extract neutral to litmus; the acid constituents amounted to 2 per cent. and the benzene extract was as low as 0.2 per cent.

H. M. D.

Action of Sulphur on Carbon Tetrabromide. A. VON BARTAL (*Ber.*, 1905, 38, 3067—3071).—When carbon tetrabromide and flowers of sulphur are heated together, a liquid distils over when the bath is at 180—195°, and an indigo-blue residue consisting of the compound $C_9Br_4S_4$, previously described by Hell and Urech (*Abstr.*, 1883, 907), together with free carbon, is left in the flask. The blue compound is purified by extraction with ether, alcohol, and carbon disulphide and subsequent solution in phenol and precipitation with alcohol. The yield is only 1.5—2 grams per 100 of tetrabromide.

The distillate contains carbon disulphide, bromine, and Hell and Urech's carbothiohexabromide, $C_2Br_6S_3$. Sulphur bromide is also probably formed.

J. J. S.

New Method of Preparation of Neon, Krypton, and Xenon. SIEGFRIED VALENTINER and R. SCHMIDT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 38, 816—820).—The apparatus consists of a cylindrical tube of 100 c.c. capacity, the volume of which can be altered by admitting mercury from below; it is connected by means of capillary tubes provided with stopcocks with (a) a small reservoir containing cocoanut charcoal, (b) a vessel in which the neon is to be collected, (c) a pipette containing argon free from chemically active gases, and (d) the mercury pump. The inert gaseous mixture is admitted into the apparatus and the charcoal reservoir cooled in liquid air. After 10—15 minutes, the stopcock on the tube leading to the charcoal reservoir is closed, and, by allowing mercury to enter the cylindrical tube, the unabsorbed neon is forced into the reservoir. The neon can be freed from helium by bringing the gas into contact with fresh charcoal cooled in liquid air and pumping off the gas which remains unabsorbed. The gas which escapes from the charcoal when the reservoir is allowed to return to the ordinary temperature is pure neon.

For the separation of krypton and neon, the apparatus is provided with two charcoal tubes, one of which is cooled to -120° after the inert gaseous mixture has been introduced into the apparatus. The whole of the krypton and xenon and some argon are absorbed, but the latter is completely removed when connection is established with the second reservoir cooled in liquid air. On allowing the temperature to rise from -120° to -80° , pure krypton is evolved. At $-15-0^\circ$, xenon mixed with some krypton escapes. To remove the krypton from this mixture, it is first absorbed by charcoal cooled in liquid air. Connection having been made with the second charcoal reservoir cooled to -180° , the greater portion of the absorbed gas is removed by warming the first reservoir to 20° . The remaining gas, which escapes on heating gently with the free flame, consists of pure xenon.

H. M. D.

Action of Weak Acids on Metallic Chlorides. ALFRED BENRATH (*J. pr. Chem.*, 1905, [ii], 72, 238—243).—The author has investigated the composition of the salts obtained on treating chlorides of the alkali metals and of the alkaline earths with sulphuric, oxalic, tartaric, and phosphoric acids. The products obtained from the interaction in aqueous solution are not necessarily the same as those from alcoholic solution. As a rule, the less soluble salt is precipitated, but if this is the salt of the weaker acid, unless its solubility is extremely small, its precipitation may be prevented in aqueous solution by the solvent action of the stronger acid. In alcoholic solution, the differences between the extents to which the different acids are dissociated are much smaller than in aqueous solution, the solvent power of the stronger acid is diminished greatly, and the salts are precipitated strictly according to their solubilities (compare also this vol., i, 734).

G. Y.

Complex Compounds of Carbonic Acid with Heavy Metals. ROBERT LUTHER and B. KRŠNĀVI (*Zeit. anorg. Chem.*, 1905, 46, 170—173).—A large number of heavy metals form complex anions with alkali hydrogen carbonates. The compounds formed have been long known as “double compounds” and are formed by treating the hydroxide or carbonate of the metal with alkali hydrogen carbonate or by adding an excess of alkali hydrogen carbonate to the solution of the metallic salt. The precipitate at first formed dissolves in excess of the precipitant, and from this fact alone it might have been inferred that there is formation of complex undissociated salts.

The intensely coloured solutions of the carbonate derivatives of bivalent copper, ferric iron, and uranyl diffuse through parchment and are therefore not colloidal; the metal always migrates to the anode.

Preliminary measurements of *E.M.F.* show that the copper complex probably consists of one cupric ion and two HCO_3 ions.

In addition to the above metals, magnesium, chromium, cobalt, and nickel appear to some extent to yield complex anions with alkali hydrogen carbonates (compare W. C. Reynolds, *Trans.*, 1898, 73, 262).

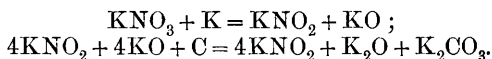
D. H. J.

Electrolysis of the Fused Nitrates of Potassium, Sodium, and Lithium. ALEXIS BOGORODSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 703—759).—The author has determined the products formed during the electrolysis under different voltages of the fused nitrates of potassium, sodium, and lithium at temperatures near their solidification points, the cathodes used being of aluminium and graphite and the anodes of platinum. The anode gases consist entirely of oxygen and nitrogen peroxide, and the solid products are mixtures of the oxides and nitrites of the metals. When potassium nitrate or sodium nitrate is electrolysed at a voltage varying between 5 and 35, the fused salt around the cathode turns yellow or orange-red, a yellow precipitate which is formed dissolving in the fused salt. This colour is supposed by the author to be due to the formation of higher peroxides of the metals. With fused lithium nitrate, the orange-red colour appears at the anode, and, if the *E.M.F.* exceeds 6 volts, metallic lithium is deposited on the cathode. The gas evolved at the anode is a mixture

of 1 mol. of oxygen with 2 mols. of nitrogen peroxide ($O_2 + 2NO_2$), but the ratio of alkali oxide to alkali nitrite in the liquid surrounding the cathode varies with the cathode material, as shown in the following table :

	$K_2O : KNO_2$	$Na_2O : NaNO_2$	$Li_2O : LiNO_2$
Graphite cathode.....	1 : 2	1 : 1.6	1 : 1
Aluminium cathode ...	1 : 1	1 : 0.8	1 : 1

From these ratios the author concludes that when a graphite cathode is used the lithium separated at the cathode is oxidised to Li_2O , whilst with potassium the oxidation proceeds as far as the formation of KO , which then undergoes further change :



With aluminium cathodes, only the first of these changes occurs. Sodium nitrate occupies a position intermediate between those of the other two nitrates.

T. H. P

Decomposition and Preservation of Sodium Hyposulphite as Anhydrous Powder and in Aqueous Solution. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1905, [iii], 33, 931—944. Compare Bernthsen, this vol., ii, 240. Bazlen, *ibid.*).—When exposed in a thin layer to the action of moist air, powdered anhydrous sodium hyposulphite is completely decomposed in seven days, but is practically stable in a closed vessel or in dry air, the slow changes observed, 10 and 4 per cent. loss of sodium hyposulphite respectively in two months, being due to admission of moisture in removing the daily samples.

Solutions of sodium hyposulphite in boiled distilled water in closed vessels decompose at rates varying with the concentration ; 25, 10, and 3 per cent. solutions are decomposed in three, eleven, and thirty-seven days respectively. The rate of change is accelerated by rise of temperature or by exposure of the solution to the air ; in the latter case, the relative stabilities are reversed, a 3 per cent. solution decomposing entirely in one, a 20 per cent. solution in two days.

Chloral and quinol, the latter when present in such small quantities as are found to protect sodium sulphite from oxidation, have no influence on the stability of sodium hyposulphite solutions. The influence of some alkaline substances, aldehydes, and other substances used in photographic developers on a 3 per cent. solution of sodium hyposulphite is exemplified in the following table (p. 707). The figures in brackets after the number of days are the percentages of hyposulphite unchanged at the end of the experiment ; in other cases, decomposition is complete at the end of the number of days given.

The decomposition of sodium hyposulphite takes place according to the equations : $3Na_2S_2O_4 = 2Na_2S_2O_3 + Na_2S_2O_6$; $Na_2S_2O_4 + O = Na_2SO_3 + SO_2$, sodium hydrogen sulphite being formed in aqueous solution. The chief product of the reaction is the sulphite.

Substance added.	Grams per litre added.	No. of days.	Substance added.	Grams per litre added.	No. of days.
NaOH	10—100	5	Sodium silicate (syrup)	25	5
Na ₂ CO ₃	2	4	Acetaldehyde (c.c.)	100	23 (0.9)
„	100	11	„	30	28 (5.9)
K ₂ CO ₃	5—200	8	Formaldehyde „	100	21
NH ₃ (c.c.)	10—200	4	„	50	28 (14.9)
Trisodium phos- phate ...	5	3	„	200	28 (8.1)
„	50	6	Trioxymethylene + Na ₂ SO ₃	10 + 1	28 (26.5)
„	100	24	„	50 + 3	28 (24.4)
Acetone + Na ₂ SO ₃ ..	5 + 15	5	Hexamethylene- tetramine	100	28 (17.5)
„	20 + 60	7	Benzaldehyde	25	4
„	40 + 120	4	„	50	19
Aniline	100	4	Acetone	50	2
Methylamine	10	4 (0.9)	„	100	5
Sodium hydrogen phosphate	50	5	„	200	6
„	100	7			

G. Y.

Rubidium Fluorides. HANS EGGELING and JULIUS MEYER (*Zeit. anorg. Chem.*, 1905, 46, 174—176).—*Rubidium fluoride*, RbF, forms a crystalline mass, very soluble in water; freezing-point measurements prove it to be unimolecular and almost completely dissociated. It forms many double salts. *Rubidium silicofluoride*, Rb₂SiF₆, is a heavy, white powder insoluble in water. *Hydrogen rubidium difluoride*, HRbF₂, is a crystalline, very hygroscopic mass; the aqueous solution probably contains the ions Rb' and HF₂'. Fairly stable salts of the formulæ H₂RbF₃ and H₃RbF₄ also exist. D. H. J.

Preparation of Ammonium Dichromate. R. SEGALLE (*Chem. Centr.*, 1905, ii, 444—445; from 41 *Jahresb. d. gr. or. Oberrealschule Czernowitz*, 1904—1905).—Potassium or sodium dichromate (1 mol.) is heated in aqueous solution with ammonium chloride (2 mols.) until the liquid assumes a deep garnet-red colour. After evaporating to half its bulk, the solution deposits in one or two days deep garnet-red, needle-shaped crystals of ammonium dichromate, which at a red heat burst into flame with evolution of ammonia and water vapour. Ammonium dichromate, which is very soluble in water, may be separated from potassium dichromate and ammonium chloride by precipitating it from solution by means of alcohol, but some of it is reduced in the process.

[With LANGER.]—Reichard's method of estimating chromic acid by means of arsenious oxide (compare Abstr., 1900, ii, 691) is modified by reducing the ammonium dichromate in concentrated acid solution in the cold, diluting with water, adding excess of sodium hydrogen carbonate, and titrating back with iodine, keeping a stream of carbon dioxide bubbling through the solution. P. H.

Action of Silver Nitrate and Thallous Nitrate on Certain Natural Silicates. GEORGE STEIGER (*Bull. U.S. Geol. Surv.*, 1905, No. 262, 75—90); FRANK W. CLARKE (*Zeit. anorg. Chem.*, 1905, 46, 197—207).—Clarke and Steiger (Abstr., 1903, ii, 380) have shown

that the alkali and alkaline earth metals of many minerals may be replaced by ammonium, and Steiger (Abstr., 1902, ii, 561) has obtained silver derivatives of analcite and chabazite. In the experiments now described, the finely-powdered minerals were mixed with various amounts of silver nitrate or thallous nitrate and heated in sealed tubes at temperatures somewhat above the melting points of the nitrates; the fused masses were extracted with water and the residues analysed. The products obtained are crystalline, and contain heavy metals in place of the alkali or alkaline earth metals of the original minerals.

Analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) yields the product $\text{AgAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, which is snow-white and optically isotropic like the original mineral. This silver-analcite is decomposed by nitric acid, but not by sodium carbonate solution; when digested with sodium thiosulphate solution, it is reconverted into the original sodium compound. The thallium derivative of both analcite and leucite (KAlSi_2O_6) approximates to $\text{TlAlSi}_2\text{O}_6$ in composition. Analcite, when heated in a sealed tube with a lead nitrate solution, has part of the sodium replaced by lead.

Similar results were obtained with several other zeolites (thomsonite, chabazite, stilbite, natrolite, scolecite, and mesolite), the replacement of the alkali or alkaline earth metal by heavy metals being more or less complete in each case. Pectolite is attacked by silver nitrate, but the product is not simple in composition; *eläolite* and *ægirite* are only slightly acted on.

L. J. S.

Preparation of Metallic Calcium in the Laboratory. PAUL WÖHLER (*Zeit. Elektrochem.*, 1905, 11, 612—618).—Calcium chloride (100 parts) and calcium fluoride (17 parts) are fused together in an iron crucible 20 cm. wide and 11 cm. deep. An anode of graphite or amorphous carbon and a cathode of iron rod, 8 mm. in diameter, are used. The distance between the electrodes should be less than their distance from the wall of the crucible, otherwise the latter acts as an intermediate conductor and is perforated by the action of the chlorine at the place where it acts as anode, and gives rise to the formation of a calcium-iron alloy at the place where it acts as cathode. The temperature of the electrolyte must lie between its own melting point (660°) and that of calcium (800°). It deteriorates in time, becoming viscid, probably owing to the formation of hydrated oxychloride; hydrogen is then liberated at the cathode and the yield decreases. The cathodic current density may vary from 50 to 250 amperes per sq. cm. The anodic current density should not exceed about 5.6 amperes per sq. cm. Chlorine is not liberated during the electrolysis; the author supposes that it combines with the carbon of the anode. The cathode touches the surface of the electrolyte and is raised as the calcium forms, so that a stick of solid metal is produced. With a current of 40 amperes, from 33 to 38 volts are required. The current efficiency is over 80 per cent. The metal contained a minute trace of iron, but was otherwise pure; its specific gravity was 1.51.

T. E.

Solubilities in Mixed Solvents. III. Solubility of Calcium Hydroxide in Aqueous Glycerol. WALTER HERZ and M. KNOCH (*Zeit. anorg. Chem.*, 1905, **46**, 193—196. Compare Abstr., 1904, ii, 709; this vol., ii, 510).—The solubility of calcium hydroxide in aqueous glycerol increases rapidly with increasing percentage of glycerol. It is suggested that for the authors' experiments on solubilities in mixed solvents the expression $(S+A)W/(S+A+W)$ has a constant value, where S is the number of grams of substance in 100 c.c. of solution, A the corresponding quantity of acetone or glycerol, and W the quantity of water, but the experimental material is not yet sufficient to establish the constancy. D. H. J.

Compounds of Haloid Salts of Metals with Hydroxylamine. G. N. ANTONOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 476—483).—The author has prepared and analysed the following double salts, which were obtained crystalline by deposition from aqueous alcoholic solution: $\text{MgCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$; $2\text{CaCl}_2 \cdot 3\text{NH}_2 \cdot \text{OH} \cdot 6\text{H}_2\text{O}$;
 $2\text{CaCl}_2 \cdot 5\text{NH}_2 \cdot \text{OH} \cdot 4\text{H}_2\text{O}$;
 $\text{CaCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH} \cdot \text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH}$;
 $4\text{CaCl}_2 \cdot \text{NH}_2 \cdot \text{OH} \cdot 20\text{H}_2\text{O}$;
 $2\text{SrCl}_2 \cdot 5\text{NH}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$; $2\text{SrCl}_2 \cdot 9\text{NH}_2 \cdot \text{OH} \cdot 3\text{HCl} \cdot \text{H}_2\text{O}$;
 $\text{BaCl}_2 \cdot \text{NH}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$.

Aqueous solutions saturated at 20° contain: about 1 per cent. of $\text{ZnCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH}$; about 1 per cent. of $\text{CdCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH}$; 44.4 per cent. of $\text{MgCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$ or 56.6 per cent. of $\text{CaCl}_2 \cdot 2\text{NH}_2 \cdot \text{OH} \cdot \text{H}_2\text{O}$. T. H. P.

"Setting" and "Hardening" of Cement. EDUARD JORDIS (*Bull. Soc. chim.*, 1905, [iii], **33**, 1029—1032).—The present position of the chemistry of this subject is discussed; the conclusions are indicated which may legitimately be drawn from the facts so far established experimentally, and it is pointed out that the principal problems have only been solved approximately. T. A. H.

Changes of Colour caused by the Action of Certain Rays on Glass. CHARLES E. RUEGER (*J. Amer. Chem. Soc.*, 1905, **27**, 1206. Compare Avery, this vol., ii, 589).—Colourless glass which is allowed to remain for some years exposed to the sun's rays in the northern part of the Butte District, Montana, U.S.A., becomes violet. This district contains large ore deposits, in which manganese dioxide is a prominent constituent. It is suggested that the colour may possibly be due to the proximity of the manganese ore, but is more probably due to manganese originally present in the glass. In any case, it is proved that the production of this violet coloration is not confined to the tropics. E. G.

Physical Properties of Glass as Functions of the Chemical Composition. EBERHARD ZSCHIMMER (*Zeit. Elektrochem.*, 1905, **11**, 629—638).—A résumé of the researches which have been made at the glass-works of Messrs. Schott, in Jena. The greater part of the results has been published already. From unpublished experiments

of Schott and Abbe, it is shown that the addition of the oxides of lithium, zinc, barium, or lead to boron trioxide glass increases the refractive index. The increase is not proportional to the quantities added, the ratio decreasing for the first two oxides and increasing for the last two as the quantity added increases. The same behaviour is observed when the oxides of sodium, zinc, barium, or lead are added to quartz glass. The oxide with the greater molecular weight gives the greater increase in refractive index. The addition of boron trioxide to a potassium silicate glass first increases the refractive index and then diminishes it. The author's own experiments on the hygroscopic qualities of glass show that all glasses which contain alkalis absorb water from steam at about 80° ; lime, zinc oxide, baryta, and especially boron trioxide diminish the tendency to absorb water.

T. E.

Atomic Weights of Carbon and Glucinum. CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1905, **27**, 1204—1206; *Zeit. anorg. Chem.*, 1905, **46**, 215—216).—It is pointed out that the determinations of the equivalent of glucinum (*Abstr.*, 1904, ii, 658) having been made with two compounds containing the same elements, the atomic weight of glucinum could, from the data obtained, be calculated independently of the carbon, and that the atomic weight of carbon could also be obtained independently of that of glucinum. Calculating by means of simultaneous equations, the atomic weight of glucinum was found to be 9.112 as compared with 9.113 previously given, whilst the atomic weight of carbon was found to be 12.007.

E. G.

Alloys of Magnesium with Tin and with Lead. NICOLAI S. KURNAKOFF and N. J. STEPANOFF (*Zeit. anorg. Chem.*, 1905, **46**, 177—192).—A complete fusion diagram has been constructed for the alloys, and the results have been confirmed by a microchemical investigation.

Magnesium-tin Alloys (compare Grube, this vol., ii, 636).—The fusion curve shows eutectic points at 8.55 atomic per cent. of magnesium and 203.5° , and at 88 atomic per cent. of magnesium and 580° ; there is a maximum or dystectic point at 795° , showing the formation of the compound Mg_2Sn , which thus has a melting point above that of magnesium (650°). Magnesium stannide, Mg_2Sn , forms crystalline aggregates which show well-marked octahedral cleavage, so that tin-magnesium alloys are brittle owing to its presence. Its sp. gr. is 3.591 at $20^{\circ}/4^{\circ}$. Its hardness, 3.5, is greater than that of the constituents. The streak is grey. The atomic lowering of the freezing point of tin by magnesium agrees with the value calculated from van't Hoff's formula, and shows the absence of solid solutions.

Magnesium-lead Alloys.—The fusion curve shows eutectic points at 15.73 atomic per cent. of magnesium and 253° , and at 80 atomic per cent. of magnesium and 475° ; there is a dystectic point at 550° , marking the existence of the compound magnesium plumbide, Mg_2Pb (compare Grube, this vol., ii, 320).

D. H. J.

Relation of Lead Iodide to Water and Oxygen. M. A. SCHTSCHERBAKOFF (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 682—699).—The electrochemical investigation of fused lead iodide by Czepinski (Abstr., 1899, ii, 267), Helfenstein (Abstr., 1900, ii, 383), Garrard (Abstr., 1901, ii, 54), and Auerbach (Abstr., 1901, ii, 590) shows that this salt exhibits abnormal behaviour as regards Faraday's law, and as regards the relation between the polarisation *E.M.F.* and heat of formation, &c. The author finds that these abnormalities are due to the fact that fused lead iodide absorbs oxygen from the air forming an oxyiodide, the amount of which may correspond with more than 30 per cent. of the iodide. This action proceeds with increased rapidity in presence of metallic lead. When heated in a current of steam, lead iodide also undergoes change according to the equation $\text{PbI}_2 + \text{H}_2\text{O} = \text{PbI}\cdot\text{OH} + \text{HI}$; boiling water has a similar, although slower, action. In a current of carbon dioxide, lead iodide is stable and can be sublimed without change. T. H. P.

Relation of Lead Iodide to Water and Oxygen. ALEXIS BOGORODSKY (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 699—702. Compare preceding abstract).—The author considers the formation of insoluble basic compounds by hydrolytic decomposition of salts in solution as due to polymerisation changes. The phenomenon is discussed in reference to the following six factors: (1) the affinity between the simple molecules of the dissolved substance—its tendency to polymerise; (2) the tendency of water to polymerise; (3) and (4) the affinity between the two products of hydrolysis and water; (5) and (6) the polymeric force of the hydrolytic products. T. H. P.

A New Cause of Dissociation of Mercuric Chloride. HENRI VITENET and CHENU (*Bull. Soc. chim.*, 1905, [iii], **33**, 944—945. Compare this vol., ii, 35).—It is shown that the amount of precipitate obtained on adding a solution of mercuric and ammonium chlorides to various natural waters is in each case proportional to the temporary hardness of the water, and that no precipitate is obtained if the water is boiled before addition of the reagents. G. Y.

Isolation of Terbium. GEORGES URBAIN (*Compt. rend.*, 1905, **141**, 521—523).—The author has separated 7 grams of the oxide of the rare element Z_δ (compare Lecoq de Boisbaudran, Abstr., 1896, ii, 249; Demarçay, Abstr., 1900, ii, 656; Urbain, this vol., ii, 35) from all traces of gadolinium by fractional crystallisation of the double nitrates of the rare earths and of nickel, and, finally, by fractional precipitation with ammonia. The element thus isolated, to which the name *terbium* should be restricted, exhibits an absorption band $\lambda = 488$; a solution of its chloride gives the beautiful green fluorescent spectrum of Lecoq de Boisbaudran's Z_β (compare Abstr., 1886, 666); the pure oxide does not exhibit phosphorescence, but when mixed with gadolinium oxide it gives the green phosphorescence of Crookes' G whilst alumina containing only 0.5 per cent. of terbia gives a magnificent white phosphorescence. The atomic weight of terbium, determined by estimating the water in the hydrated sulphate, is 159.2 ($\text{O} = 16$); the oxide is

brown or black, according as it is prepared from the oxalate or sulphate by calcination. The salts of terbium are colourless, and are slightly more soluble than the corresponding salts of gadolinium.

M. A. W.

Preparation of Metallic Aluminium. HEINRICH F. D. SCHWAHN (D.R.-P. 160286).—Aluminium may be prepared by the action of reducing gases on aluminium sulphide. A more convenient method is that of heating porous aluminium sulphate (prepared by calcining crystallised aluminium sulphate with a little sodium chloride and breaking up the mass) at 800—900° in a stream of carbon monoxide or other reducing gas containing 5 per cent. of carbon disulphide. Porous aluminium oxide or a mixture of aluminium sulphate with charcoal may be employed in place of the porous sulphate. A vertical graphite furnace is used.

C. H. D.

Alloys of Copper and Aluminium. LÉON GUILLET (*Rev. de Metallurgie*, 1905, 2, 567—588).—The freezing point curve of alloys of copper and aluminium shows two maxima corresponding with the compounds AlCu_3 and Al_2Cu respectively. The existence of a compound AlCu is also indicated. The micrographic examination of the alloys shows seven constituents, α , β , γ , δ , ϵ , η , and H . The constituent α is a solid solution of aluminium in copper containing from 0 to 8 per cent. of aluminium. The constituents β and γ consist chiefly of the compound AlCu_3 , the former being found in slowly cooled alloys and the latter in specimens quenched above 525°. The solid solution δ is intermediate in composition between AlCu_3 and AlCu ; ϵ seems to be pure AlCu and η to be pure Al_2Cu . H is either pure aluminium or a solid solution containing a very small percentage of copper. The influence of quenching from different temperatures on the physical properties and micro-structure is described.

Alloys consisting only of the solution α (aluminium bronzes) are malleable and ductile; the presence of β causes hardness and brittleness, 11 per cent. of aluminium being the limiting composition for industrially valuable alloys.

C. H. D.

A New Isomeric Modification of Aluminium Hydroxide. DONATO TOMMASI (*Chem. Centr.*, 1905, ii, 605; from *Rev. gén. chim. pure appl.*, [vii], 8, 246—247).—After about three months in contact with water, ordinary aluminium hydroxide, prepared by precipitation from aluminium salt solutions with ammonia, changes into a new δ -modification, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which is easily soluble in concentrated sulphuric acid, but resembles ignited aluminium hydroxide in its slight solubility in hydrochloric, nitric, or acetic acids or in aqueous alkali hydroxides. It does not form an oxychloride with aluminium chloride. If the oxychlorides, $2(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}) \cdot 3\text{Al}_2\text{Cl}_6$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \cdot 4\text{Al}_2\text{Cl}_6$, which are formed by the action of aluminium on cupric chloride in 30 and 8 per cent. solutions respectively are boiled with aluminium until cessation of the evolution of hydrogen, the oxychloride, $6(\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}) \cdot \text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, is formed in nacreous leaflets. On adding concentrated sulphuric acid or certain salts to the aqueous

solution of this, it coagulates with formation of δ -aluminium hydroxide.
G. Y.

"Aluminium Carbonicum." A. GAWALOWSKI (*Chem. Centr.*, 1905, ii, 743—744; from *Pharm. Post*, 1905, 38, 405).—The aluminium carbonate previously prepared by the author (*Chem. Centr.*, 1905, i, 1584) is not the normal carbonate; it contains 40—45 per cent. Al_2O_3 , 8—9 per cent. CO_2 , and water which is in different states of combination.
H. M. D.

Plasticity of Clays. FRANK F. GROUT (*J. Amer. Chem. Soc.*, 1905, 27, 1037—1049).—It is pointed out that the property of plasticity involves two factors, namely, strength and the amount of deformation possible before crumbling. In the experiments described, the strength was determined by finding the weight required to force a Vicat needle of 7 sq. cm. section into the clay to a depth of 3 cm. in half a minute. The deformation, or amount of possible flow, was determined by measuring the increase in the area of the head of a cylinder of the moist clay, 5 cm. long and 2 cm. in diameter, when the cylinder was compressed to the point of fracture. The product of these two factors was regarded as the measure of plasticity at the particular stage of wetness of the clay. As the mass dried, a maximum plasticity was observed when the clay contained a certain definite proportion of water.

By employing this method, attempts have been made to ascertain the causes of plasticity and have led to the following conclusions. Plasticity is not much affected by the presence of a small proportion of sand, but when the grains of sand are sufficiently numerous to come into contact with one another, both the strength and the amount of flow are diminished. It was found that on addition of 0.08 per cent. of agar-agar, the plasticity of two clays was increased from 7 and 11 to 11 and 15 respectively, whilst it required an amount of alumina cream (calculated as Al_2O_3) equal to 3 per cent. of the weight of the clay to increase the plasticity to the same extent. Plasticity is also increased by the fineness of the clay and by the presence of plane surfaces (small plates) in the mass, which increase both the amount of possible flow and the strength. The increase in plasticity by weathering is attributed chiefly to mechanical action, but may be due to some extent to addition of colloidal substances by the action of bacteria. It is concluded that molecular attraction is the chief cause of the high degree of plasticity of clays.
E. G.

Composition of a Cannon Ball from the Moat of the Bastille. A. PORLIER (*Rev. de Métallurgie*, 1905, 2, 793—794).—A cannon ball, one of a number discovered in the former moat of the Bastille, was found to be entirely compact and metallic in appearance, but to give a greenish-yellow fracture. The sp. gr. was only 4.854. Analysis showed it to contain Fe 72.0, C 5.9, Si 0.25, Mn 0.75, O 17.45, H_2O 2.9 per cent. On microscopical examination, the original structure of white cast iron was found to be perfectly preserved, the cementite being brilliant and intact, whilst the pearlite had been

replaced by ferric oxide. The replacement had thus been completed by diffusion to a depth of 5 cm., the radius of the ball being 10 cm., in a century or less. The high carbon content is due to a part of the iron having diffused outwards into the surrounding earthy crust.

C. H. D.

Colloidal Ferric Hydroxide. III. Influence of Various Salts on the Coagulation. A. V. DUMANSKY (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 502—507. Compare this vol., ii, 37 and 393).—Colloidal ferric hydroxide solutions are coagulated by aqueous solutions of potassium, barium, silver, cupric, manganese, or lead nitrate, cupric or ammonium chloride, sodium carbonate or magnesium sulphate, and these solutions undergo an increase in their electrical conductivity on mixing with the colloidal liquid. On the other hand, solutions of mercurous, mercuric, or aluminium nitrate, mercuric acetate, or ferric chloride, which effect no coagulation of colloidal ferric hydroxide solutions, have their conductivity diminished on being mixed with the latter. From this behaviour, the author concludes that coagulation of colloidal ferric hydroxide is only produced by those salts which are less soluble in the colloidal solution than in water.

T. H. P.

Iron Sulphides and the Purification of Coal Gas from Hydrogen Sulphide. L. GEDEL (*Chem. Centr.*, 1905, ii, 445—447; from *J. Gasbel.*, 1905, 48, 400—407).—(1) Iron heated at 450—500° with excess of sulphur forms ferric disulphide, FeS_2 ; this substance loses sulphur on heating to 700°, giving Fe_2S_3 ; heated to above 700°, it is converted into ferrous sulphide, FeS . (2) Excess of freshly-prepared ammonium sulphide added to a solution of ferric chloride produces iron sesquisulphide, which, with hydrochloric acid, decomposes according to the equation $\text{Fe}_2\text{S}_3 + 4\text{HCl} = 2\text{FeCl}_2 + 2\text{H}_2\text{S} + \text{S}$, and is oxidised by moist air as follows: $\text{Fe}_2\text{S}_3 + 3\text{O} = \text{Fe}_2\text{O}_3 + 3\text{S}$. (3) If ferric chloride is treated with ammonium sulphide in sufficient quantity to allow the solution still to remain acid by virtue of the hydrolysis of the iron salt, sulphur is precipitated and a black colour is developed. The product of this reaction has, before drying, the composition $2\text{FeS} + \text{S}$; if, however, it is dried above 100°, it contains some disulphide formed as follows: $2\text{FeS} + \text{S} = \text{FeS}_2 + \text{FeS}$. If sufficient ammonium sulphide is added to render the ferric chloride solution alkaline, the dried precipitate contains chiefly the sesquisulphide together with small quantities of ferrous sulphide, sulphur, and ferric disulphide. (4) Ferrous sulphide added to ammonium polysulphide produces iron sesquisulphide. (5) A small amount of ammonium sulphide added to an alkaline solution of an iron salt, obtained by adding ammonia to ferric chloride containing tartaric acid, produces iron sesquisulphide. (6) Hydrogen sulphide acts on dried ferric hydroxide, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, in the presence of hydrochloric acid to form ferrous sulphide, sulphur, and ferric disulphide. (7) Hydrogen sulphide, mixed with a small quantity of ammonia, converts ferric hydroxide into the sesquisulphide. (8) The former product, exposed to the air after the completion of the oxidation, contains the disulphide unchanged; the latter, on the other hand, is completely oxidised to ferric oxide and

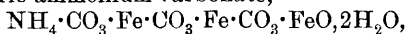
sulphur; in each case a small amount of ferric sulphate is also formed, the amount being independent of the presence of moisture, but increasing with rise of temperature. (9) The admixture of air with hydrogen sulphide containing traces of hydrogen chloride exerts no influence on the formation of ferric disulphide. (10) Gas purifiers contain the sesquisulphide, but not the mono- or di-sulphides of iron.

In the purification of coal gas, the action may be expressed by the equation $\text{Fe}_2(\text{OH})_6 + 3\text{H}_2\text{S} = \text{Fe}_2\text{S}_3 + 6\text{H}_2\text{O}$. The formation of the disulphide is prevented by the presence in the gas of traces of ammonia. The sulphide Fe_7S_8 behaves towards hydrochloric acid like a compound of the formula $6\text{FeS}, \text{FeS}_2$, giving the disulphide with evolution of hydrogen sulphide

P. H.

New Class of Iron Compounds. OTTO HAUSER (*Ber.*, 1905, **38**, 2707—2710).—The precipitates formed on adding ammonium carbonate to solutions of ferrous or of ferric salts are soluble in an excess of the reagent. The ferric solution thus prepared is a blood-red liquid from which the iron is precipitated by hydrogen sulphide, or by reagents which react with carbonates, or by boiling alkali hydroxides, but not by potassium ferrocyanide, whereas Prussian blue dissolves in aqueous ammonium carbonate to form a violet-red solution. The ferric ammonium carbonate solution is stable in a closed vessel for several weeks, but deposits ferric hydroxide on evaporation.

The white ferrous precipitate is less easily soluble in excess of ammonium carbonate, forming a colourless solution which, on treatment with hydrogen peroxide or on free exposure to air, rapidly becomes brown, but when oxidised by a limited quantity of air it deposits a basic ferrous-ferric ammonium carbonate,



which forms stellate aggregates of small, doubly refracting, green prisms, and on exposure to air becomes olive-green and finally brown, owing to formation of ferric hydroxide. It dissolves with evolution of carbon dioxide in dilute acids to form yellowish-green solutions, and when treated with alkali hydroxides yields ammonia and a black, strongly magnetic ferrous-ferric oxide.

The olive-green powder formed on partial oxidation of the basic salt contains ferrous and ferric iron in the proportion 1 : 1. G. Y.

Iron and Chromium Nitrides. EMIL BAUR and GERARDUS L. VOERMAN (*Zeit. physikal. Chem.*, 1905, **52**, 467—478).—Under no conditions could a direct combination of iron and nitrogen be observed. The tension of iron nitride is too great to be determined; at temperatures between 500° and 600° , it is certainly greater than 15 atmospheres. In these circumstances, the authors' study of the equilibrium $\text{iron} + \text{ammonia} \rightleftharpoons \text{iron nitride} + \text{hydrogen}$ does not throw much light on the dissociation of ammonia, the calculation of which was one of the chief objects of the investigation.

The tension of chromium nitride at high temperatures has been measured, but it has been observed that the dissociation does not proceed until a definite dissociation pressure has been reached, and then cease; on the contrary, the dissociation pressure exhibits a

continuous, if slow, increase, and the view is adopted that chromium and chromium nitride form, not two constant phases, but one variable phase (compare Muthmann and Baur, *Abstr.*, 1903, ii, 213). In these circumstances, the tensions of chromium nitride determined by the author are only approximate; at 800° , for example, the tension is about 100 mm. Chromium nitride is much more stable than iron nitride, and is not reduced in a current of hydrogen, even at a pressure of 13 atmospheres. It is noteworthy that chromium is very efficient as a catalytic agent in the decomposition of ammonia, whilst it has no effect whatever in promoting the synthesis of ammonia; it is possibly a one-sided catalytic agent. J. C. P.

Solubilities of the Isomeric Chromic Chlorides. H. W. BAKHUIS ROOZEBOOM and J. OLIE, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, 8, 66—70).—Since the isomeric chromic chlorides may be estimated in each other's presence (see Werner and Gubser, *Abstr.*, 1901, ii, 453), and require in solution much more time to get into equilibrium with each other than is necessary for the establishment of equilibrium between solid and solution, it is possible to study the change of solubility resulting from the gradual transformation which goes on in the solution.

The final condition of chromic chloride solutions of various concentrations at 25° has been determined, and it is found that both the green and the violet salts lead to the same condition of equilibrium. In weak solutions, the chromic chloride at the point of equilibrium occurs almost exclusively in the violet modification. As the concentration increases, the equilibrium shifts more and more in favour of the green modification.

The solubilities also of the green and violet salts have been determined at 25° . The solubility in each case increases as time goes on owing to the transformation green \rightarrow violet, or violet \rightarrow green, as the case may be. When the two solubility lines are represented on the same diagram as the equilibrium curve, it is seen that the latter intersects the solubility line for the green salt, hence the violet chromic chloride cannot be definitely in equilibrium at 25° with any solution; that is, the green salt is the stable modification at that temperature. The precipitation of the violet salt by passing hydrogen chloride into solutions of the green salt previously heated to 100° is possible, because at the latter temperature the equilibrium curve cuts the solubility line for the violet salt; the change violet \rightarrow green in solution is slow enough to allow of the precipitation of the violet salt.

J. C. P.

Perchromates. KARL A. HOFMANN and H. HIENDLMAIER (*Ber.*, 1905, 38, 3059—3066. Compare *Abstr.*, 1904, ii, 410, 737; Riesenfeld, Wohlers, and Kutsch, this vol., ii, 461).—Wiede's compound, $\text{CrO}_4(\text{NH}_3)_3$ (*Abstr.*, 1898, ii, 28), is obtained when 10 per cent. aqueous ammonium hydroxide is saturated at 0° with crystallised ammonium dichromate, 30 per cent. hydrogen peroxide added to the clear solution, and the mixture kept for 6—12 hours. The large, brown crystals which separate are freed from a red, crystalline powder by allowing the temperature to rise to 10 — 15° . Its properties are those of an

ammine and not of an ammonium salt, and it is represented on Werner's

co-ordinate system as $(\text{NH}_3)_3\text{Cr} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \\ \diagup \text{O}_2 \end{array}$. An isomeride (β -compound)

is formed when a 20 per cent. solution of ammonia is saturated at 0° , first with ammonium dichromate and then with ammonia, and finally 30 per cent. hydrogen peroxide added. After some 12 hours, quadratic plates are obtained showing strong pleochroism from yellowish-brown to dirty purple. Extinction with crossed Nicols occurs parallel to the diagonals. The compound resembles its isomeride in all its more important physical and chemical properties, but differs slightly in solubility and rate of decomposition. The three ammonia groups are not removed by treatment with 40 per cent. acetic acid. Wiede's compound, $\text{NH}_4\text{CrO}_5 \cdot \text{H}_2\text{O}_2$ (Abstr., 1898, ii, 295), is readily obtained when saturated ammonium chromate solution (4 c.c.) is mixed with water (3 c.c.) and excess of crystallised ammonium nitrate at 0° and 30 per cent. hydrogen peroxide (4 c.c.) added to the clear solution at a low temperature.

Ice-cold 20 per cent. ammonia solution transforms it partly into the β -compound, and the addition of small amounts of water causes the evolution of five equivalents of oxygen and the formation of ammonium dichromate.

J. J. S.

Halogen Compounds of Molybdenum and Tungsten. ARTHUR ROSENHEIM and HANS J. BRAUN (*Zeit. anorg. Chem.*, 1905, **46**, 311—322).—The molybdenum required for the preparation of the chlorides was obtained in good yield and free from air-bubbles by a modification of the Goldschmidt process, the reaction being moderated by the addition of a flux of 50 parts of calcium fluoride for every 100 parts of molybdenum trioxide and 38 parts of aluminium, and the metal allowed to agglomerate by keeping the mass in a liquid condition for some time after the reaction.

Insoluble molybdenum trichloride, MoCl_3 , prepared according to the directions of Blomstrand and of Liechti and Kempe, has the appearance of red phosphorus. It slowly decomposes in the air with evolution of hydrogen chloride. It is quite insoluble in water and in most other solvents. It is slightly soluble in nitrobenzene, but not sufficiently to allow a molecular weight determination to be made.

By the action of a stream of gaseous ammonia on it at 340° , a black substance, $\text{Mo}_2(\text{NH}_2)_3\text{Cl}_3$, is formed, which is insoluble in dilute acids and in water, and evolves ammonia when heated with soda-lime. By employing a temperature of 760° instead of 340° , molybdenum nitride, Mo_3N_2 , is obtained as a grey, metallic powder, the properties of which have already been described by Uhrlaub. Molybdenum trichloride under the action of a solution of ammonia develops considerable heat and yields a black, easily oxidisable substance of the formula MoNH_4O_4 .

In contact with liquefied ammonia, it gives a brown product of the formula $\text{Mo}_2(\text{NH}_2)_3\text{Cl}_3 \cdot 10\text{NH}_3$, which evolves ammonia in the air and finally leaves a residue of $\text{Mo}_2(\text{NH}_2)_3\text{Cl}_3$.

Insoluble molybdenum tribromide is obtained similarly to the tri-

chloride; it forms black needles which may be sublimed. By the action of ammonia gas even at a low temperature it is reduced to metallic molybdenum.

In view of the close resemblance between insoluble molybdenum chloride and insoluble chromium chloride, an attempt was made to obtain a soluble form of chromium trichloride by the catalytic action of molybdenum dichloride, zinc chloride, &c. The attempt was unsuccessful, but the chloride has since been obtained in solution by Chilesotti, who electrolysed a hydrochloric acid solution of molybdic acid. On adding potassium fluoride to the soluble chloride, a bright violet, crystalline precipitate of the salt $\text{KMoF}_4 \cdot \text{H}_2\text{O}$ is obtained, which is insoluble in water, but is gradually decomposed by it. Similarly the salt $(\text{NH}_4)\text{MoF}_4 \cdot \text{H}_2\text{O}$ is obtained. The filtrate from the latter gives, on evaporation over sulphuric acid, violet crystals having the composition $(\text{NH}_4)_3\text{Mo}_2\text{F}_9 \cdot 2\text{H}_2\text{O}$. Molybdenum sodium fluoride was formed, but was not obtained pure.

Soluble molybdenum tribromide is obtained in a similar way to the chloride; on addition of ammonium bromide, it gives a solution from which dark red, rhombic crystals of the composition $(\text{NH}_4)_2\text{MoBr}_5 \cdot \text{H}_2\text{O}$ are obtained by evaporation.

D. H. J.

Reduction of Thorium Oxide by Boron and Silicon. EDGAR WEDEKIND and K. FETZER (*Chem. Zeit.*, 1905, 29, 1031—1032).—An intimate mixture of 10 grams of thorium oxide with 3.5 grams of crystalline silicon was heated in a magnesite crucible for seven minutes by a current of 100—110 amperes. The resulting mass, which has a metallic and crystalline appearance, is being investigated. With boron, a grey, micro-crystalline mass was obtained, which was not completely fused on further heating.

P. H.

Presence of Bismuth in Pyrites from Agordo. ARNALDO PIUTTI and E. STOPPANI (*Gazzetta*, 1905, 35, ii, 29—32).—Pyrites from the mines of Agordo contains traces of bismuth. A method for its extraction on the large scale is described.

T. H. P.

Hardness of Hammered Tantalum. WERNER VON BOLTON (*Zeit. Elektrochem.*, 1905, 11, 503—504).—The tantalum used in the experiments on hardness previously described (this vol., ii, 258) contained traces of oxide which very considerably increase its hardness. It also appears that the diamond is not suitable for drilling ductile metals. Further experiments show that the metal can be filed with a specially hard file, the edge of a very hard chisel is spoiled at each blow, a very hard drill lubricated with turpentine will perforate 1 mm. of the metal in seven to ten minutes, a steel point, hardened in water, scratches the metal, but soon becomes blunt. It appears, therefore, that tantalum combines the hardness of the best and most carefully hardened steel with sufficient ductility to allow it to be rolled or hammered.

T. E.

Tantalum and Hydrogen. M. VON PIRANI (*Zeit. Elektrochem.*, 1905, 11, 555—558).—When pure tantalum is heated in very care-

fully purified hydrogen, it absorbs a considerable quantity of the gas. At a red heat the metal takes up 0.3 per cent. of its weight, at a yellow heat 0.4 per cent. (in four to six hours), and this quantity is not increased by heating to whiteness. The volume of hydrogen absorbed is 740 times that of the metal. The wire, after taking up the hydrogen, is white with metallic lustre, crystalline, and so brittle that it may be powdered in a mortar. The electrical resistance is increased 1.7 to 2.1 times and its temperature-coefficient is decreased from 0.3 to 0.1 per cent. per degree. When the metal containing hydrogen is heated to redness in a vacuum, it loses about three-fourths of the hydrogen fairly readily. The remainder is only completely expelled by fusing the metal. The small, firmly combined residue of hydrogen (about 0.1 per cent. of the weight of the metal) is sufficient to make it brittle and to give it high electrical resistance.

The hydrogen compound is also formed when tantalum pentachloride is heated in a current of hydrogen in a hard glass tube containing a red hot platinum wire; the hydride is deposited on the hot wire.

T. E.

Double Fluorides of Tantalum. CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1905, 27, 1140—1157).—The tantalic oxide used in this investigation was obtained from the columbite of South Dakota. Potassium tantalum fluoride obtained by the addition of potassium fluoride to a solution of the mixed metallic oxides was purified by repeated crystallisation from water acidified with hydrofluoric acid, and was afterwards heated with concentrated sulphuric acid in order to remove silica. The product was boiled repeatedly with water and the white oxide thus obtained was well washed with water. The following double salts were prepared and analysed.

Tantalum lithium fluoride, $\text{LiF} \cdot \text{TaF}_5 \cdot 2\text{H}_2\text{O}$, forms monoclinic crystals [$a:b:c = 0.5703:1:1.6235$; $\beta = 87^\circ 46'$].

The tantalum sodium fluorides, $3\text{NaF} \cdot \text{TaF}_5$ and $2\text{NaF} \cdot \text{TaF}_5 \cdot \text{H}_2\text{O}$, have been prepared by Marignac (*Ann. Chim. Phys.*, 1866, [iv], 9, 247). One gram of the former salt was found to dissolve in 20.5—20.9 parts of water at 25° ; it crystallises in rhombic prisms [$a:b:c = 0.6017:1:0.2799$]. The salt $2\text{NaF} \cdot \text{TaF}_5 \cdot \text{H}_2\text{O}$ crystallises in thin plates; the mother liquor from this salt slowly deposits the double salt, $\text{NaF} \cdot \text{TaF}_5$, which crystallises in lustrous cubes of the isometric system.

The existence of the potassium salts, $2\text{KF} \cdot \text{TaF}_5$ and $2\text{KF} \cdot \text{TaO}_2\text{F}_3 \cdot \text{H}_2\text{O}$, was confirmed.

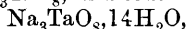
The rubidium salt, $2\text{RbF} \cdot \text{TaF}_5$, was prepared, and evidence was obtained of the existence of another tantalum rubidium fluoride richer in tantalum.

Tantalum caesium fluoride, $\text{CsF} \cdot \text{TaF}_5$, forms rhombohedral crystals [$c = 1.0467$]; the salt $2\text{CsF} \cdot \text{TaF}_5$ crystallises in small needles.

Tantalum pyridine fluoride, $3(\text{C}_5\text{H}_5\text{N} \cdot \text{HF}) \cdot 2\text{TaF}_5 \cdot 2\text{H}_2\text{O}$, forms hexagonal crystals [$c = 1.6259$]; by dissolving this salt in strong hydrofluoric acid, the salt $\text{C}_5\text{H}_5\text{N} \cdot \text{HF} \cdot \text{TaF}_5$ can be obtained, which crystallises in long, slender needles. Crystalline salts were also obtained with methylamine, ethylamine, triethylamine, and quinoline.

In addition to the salt $2\text{NH}_4\text{F}\cdot\text{TaF}_5$, described by Marignac, evidence was obtained of the existence of other tantalum ammonium fluorides.

Pertantalates can be readily prepared by the action of hydrogen peroxide on solutions of the corresponding tantalates; in this way, potassium pertantalate, K_3TaO_8 , and sodium pertantalate,



were prepared (compare Melikoff and Pissarjewsky, *Abstr.*, 1899, ii, 491). E. G.

Melting Point of Gold and Expansion of Some Gases at High Temperatures. II. ADRIEN JAQUEROD and F. LOUIS PERROT (*Arch. Sci. phys. nat.*, 1905, 20, 128—151. See this vol., ii, 627).—The results of the determinations of the melting point of gold with the silica gas thermometer previously described are recorded. The values are: nitrogen ($T_0=272.85$), 1066.9° , 1067.4° , 1067.5° , 1067.2° ; air ($T_0=272.85$), 1067.0° , 1067.4° ; carbon dioxide ($T_0=271.96$), 1066.1° , 1066.3° , 1066.7° ; oxygen ($T_0=272.66$), 1066.7° , 1066.7° , 1066.8° , 1067.1° ; carbon monoxide ($T_0=272.85$), 1067.05° . It is impossible to obtain determinations with hydrogen or with helium, as it is found that both gases diffuse through silica at high temperatures. In the case of hydrogen, it is shown that this diffusion, although absent at the ordinary temperature, becomes evident at 200° , whilst with helium it is more marked and would probably be perceptible at 100° . A determination of the melting point of gold with a porcelain nitrogen thermometer gave the value 1063.15° , but it is found that this substance also is useless for helium or hydrogen, which diffuse through at the temperature necessary. L. M. J.

Platinum Compounds. MAURICE BLONDEL (*Ann. Chim. Phys.*, 1905, [viii], 6, 81—144).—Platinic hydroxide, $\text{PtO}_2\cdot 4\text{H}_2\text{O}$, when freshly prepared by Fremy's method, is readily soluble in dilute acids or alkalis to form normal salts, and hence in this state is probably represented by the formula $\text{Pt}(\text{OH})_4\cdot 2\text{H}_2\text{O}$, two of the hydroxyl groups being acidic and two basic. When dried by exposure to air, or even when allowed to remain for some time in contact with water, the hydroxide darkens in colour and becomes insoluble in dilute acids, and is then probably represented by the formula $\text{H}_2\text{Pt}(\text{OH})_6$, and is a compound belonging to the chloroplatinic acid series. When heated, platinic hydroxide loses 2 mols. of water at 100° , forming Döbereiner's oxide, which is soluble only with difficulty in acids and alkalis, and a third mol. at 120° (compare Wöhler, *Abstr.*, 1904, ii, 44).

Platinic hydroxide dissolves in alkalis to form normal or orthoplatinates of the type $\text{Pt}(\text{OH})_4\cdot 2\text{M}'\text{OH}$, where M' is an alkali metal. These are readily soluble in water, but when heated at 100° become insoluble and less readily attacked by acids, and are then probably represented by the typical formula $\text{M}_2'\text{Pt}(\text{OH})_6$ (compare Bellucci, *Abstr.*, 1904, ii, 180). A solution of the normal sodium platinate after standing for some days becomes gelatinous owing to the separation of Weiss and Döbereiner's platinate, $\text{Na}_2\text{O}(\text{PtO}_2)_3\cdot 6\text{H}_2\text{O}$, and when dialysed for several days a solution of sodium metaplatinate, $\text{Na}_2\text{O}(\text{PtO}_2)_5\cdot 9\text{H}_2\text{O}$, is obtained. The metaplatinate can be reconverted

into orthoplatinate by the addition of alkali. Both platينات yield precipitates of platinic hydroxide on addition of acetic acid.

When platinic hydroxide is mixed with excess of dilute hydrochloric acid, it dissolves, forming a solution of the normal chloride, $\text{Pt}(\text{OH})_4 \cdot 2\text{HCl}$. This gives no precipitate on addition of a solution of a potassium salt, and yields platinic hydroxide in an amorphous form when diluted with water, and in a crystalline form when dialysed. When kept, the normal chloride in this solution rapidly passes into chloroplatinic acid.

When a solution of chloroplatinic acid is saturated with platinic hydroxide and the liquid is dialysed, there is eventually formed a product which coagulates when gently warmed or on the addition of a trace of an alkali salt. The coagulate so formed is reddish-brown and has the composition represented by the formula $(\text{PtO}_2)_5 \cdot 2\text{HCl} \cdot 9\text{H}_2\text{O}$, is slowly dissolved by hydrochloric acid, forming chloroplatinic acid, and is converted by boiling water into anhydrous *metaplatinic acid*, $(\text{PtO}_2)_5 \cdot 5\text{H}_2\text{O}$. These compounds present some analogy with the ferric compounds similarly prepared by Béchamp (*Ann. Chim. Phys.*, 1859, 296) and the metastannyl derivatives obtained by Engel (*Abstr.*, 1897, ii, 376).

When a solution of silver nitrate is added to a saturated solution of platinic hydroxide in chloroplatinic acid, a precipitate of the *salt* $(\text{PtO}_2)_4 \cdot 3\text{HCl} \cdot \text{AgCl} \cdot 4\text{H}_2\text{O}$ is formed; this, when washed with water, decomposes, yielding a solution of a platinic compound and a precipitate of silver chloride. The treatment may be repeated several times and a series of platinic compounds containing decreasing amounts of chlorine obtained.

Platinic hydroxide dissolves slowly in sulphuric acid, diluted with its own volume of water at 0° , and from the solution heavy, orange-yellow, microscopic needles of *normal platinic sulphate*, $\text{PtO}_2 \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$, separate. This loses $3\text{H}_2\text{O}$ at 100° , and is converted into the *compound* $\text{H}_2\text{PtO}_2 \cdot \text{SO}_4$, which may be regarded as a derivative of platinimono-sulphuric acid, $\text{H}_2\text{Pt}(\text{OH})_4 \cdot \text{SO}_4$.

Platinic sulphate dissolved in sulphuric acid is reduced by oxalic acid to *sesquioxyplatinisulphuric acid*, which may be represented by the constitutional formula $\text{Pt}_2(\text{OH})_6(\text{SO}_3)_4(\text{OH})_2 \cdot 8\frac{1}{2}\text{H}_2\text{O}$. It crystallises in pale yellow, triclinic prisms [$a:b:c = 1.6236:1.05492$; $\alpha = 88^\circ 55'$, $\beta = 90^\circ 29'$, $\gamma = 101^\circ 53'$] and gradually loses water when dried under reduced pressure over sulphuric acid, forming the stable, less hydrated acid $\text{Pt}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. Aqueous solutions of sesquioxyplatinisulphuric acid give no precipitate with barium chloride at first, but do so after standing for some time. The acid is dibasic. Excess of alkali precipitates from it a condensed form of hydrated *platinum sesquioxide* (compare Dudley, *Abstr.*, 1902, ii, 564), and excess of hydrochloric acid produces a mixture of platinous and platinic chlorides. The *sodium*, *potassium*, and *barium* salts are crystalline. This acid and its salts present some analogies with the complex chromium and iron compounds obtained by Recoura (*Abstr.*, 1895, ii, 501, and 1903, ii, 600).

When potassium platinoso-oxalate is oxidised with hydrogen peroxide, it is converted into *potassium platinoxalate*, $\text{K}_2\text{PtO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, which

crystallises in large, amber-yellow, rhombic tablets, is excessively soluble in water, and detonates when heated. The *free acid*, $\text{H}_2\text{PtO}(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$, is obtained by decomposing the silver salt with hydrochloric acid; it crystallises in large, amber-coloured tablets and detonates violently when heated.

The copper-coloured platinoso-oxalates are shown to contain platoso-oxalic acid and not to be isomeric with the yellow platinoso-oxalates or decomposition products of these, as has been supposed (compare Werner, *Abstr.*, 1896, i, 465; Vezes, *Abstr.*, 1899, i, 572).

A method for the estimation of platinum in platinoso-oxalates by the use of potassium permanganate is described in the original.

T. A. H.

The Oxides of Palladium. LOTHAR WÖHLER and JAMES KÖNIG (*Zeit. anorg. Chem.*, 1905, **46**, 323—349).—Of the four oxides described in the literature only two, namely, PdO_2 and PdO , are found to exist.

Palladium dioxide prepared by double decomposition is more or less impure; it is best obtained by the action of ozone on palladium salts or by the anodic electrolytic oxidation of palladium salts in nearly neutral solution, and with nitric acid as the cathodic depolariser. It is thus obtained as a dark brown product with varying amounts of combined water; the dissociation of the more highly hydrated substance is probably exothermic. When dried over sulphuric acid, its formula is approximately $\text{PdO}_2 \cdot 2\text{H}_2\text{O}$. It is unstable, and in contact even with cold water decomposes slowly into monoxide and oxygen. The dry substance is more stable, but at about 200° it is completely decomposed. Its behaviour to acids and alkalis varies with the time which has elapsed since its preparation. The substance when dried over sulphuric acid dissolves readily in nitric acid and fairly readily in sulphuric acid. When freshly precipitated, it is insoluble in dilute sodium hydroxide. It is a strong oxidising agent, and reduces hydrogen peroxide both in acid and alkaline solution.

Palladium monoxide, PdO , is best obtained by boiling a faintly acid solution of palladium nitrate with water. It separates with varying amounts of combined water, and the colour varies correspondingly from yellowish-brown to black. Dried over sulphuric acid it forms black, shining grains. At 100° , it is blackish-brown, but still contains 8 per cent. of water, which it still retains at 200° and even at 500 — 600° . It is not until it is heated to a temperature of 800 — 840° in oxygen that the quite anhydrous green monoxide is obtained. Above this temperature, the anhydrous oxide decomposes. Precipitated in the cold, the hydrated monoxide is soluble in dilute acids and in excess of alkali; precipitated hot and then boiled up in the liquid, it is no longer completely soluble even in boiling concentrated alkali hydroxides. Dried at 100° , it is insoluble in acetic acid and nearly insoluble in sulphuric or nitric acid. The completely anhydrous substance is scarcely soluble in boiling hydrochloric acid or in *aqua regia*.

D. H. J.

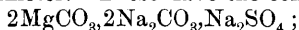
Mineralogical Chemistry.

Two Tellurium Minerals from Colorado. WILLIAM E. HILLEBRAND (*Bull. U.S. Geol. Surv.*, 1905, No. 262, 55—57).—Emmonsite? (see Abstr., 1905, ii, 97). Tetradymite in cleavage masses of considerable size, from near Whitehorn, in Fremont Co., gave the following results:

Bi.	Te.	Se.	S.	Fe ₂ O ₃ .	Insol.	Total.	Sp. gr.
52.14	46.62	0.20	0.14	0.22	0.15	99.47	7.816

L. J. S.

Tychite, a New Mineral; its Artificial Production and Relation to Northupite. SAMUEL L. PENFIELD and GEORGE S. JAMIESON (*Amer. J. Sci.*, 1905, [iv], 20, 217—224).—In a parcel of octahedral crystals of northupite ($\text{MgCO}_3, \text{Na}_2\text{CO}_3, \text{NaCl}$, Pratt, Abstr., 1897, ii, 48) from Borax Lake, San Bernardino Co., California, one crystal was, by the merest chance, found to contain sulphate in place of chloride. Further search among several thousand crystals, each one separately being tested chemically, resulted in the discovery of only three more crystals of the new mineral, to which the name *tychite* (from $\tauύχη$, “luck”) is given. The crystals are small (3 mm. diam.) and are exactly like northupite in appearance. After preliminary tests, only one crystal (weighing 11 mg.) remained, and, in order to determine the composition of the mineral, it was necessary to prepare it artificially. This was done by a similar method to that employed for the artificial production of northupite (Schulten, Abstr., 1896, ii, 610). A solution of magnesium sulphate was added to one containing sodium carbonate and sulphate and the mixture heated in a steam-bath; at the end of five days the amorphous precipitate was almost wholly converted into perfectly developed octahedral crystals, about 0.15 mm. in diameter. These have the composition



they are optically isotropic, and have a refractive index of 1.510; sp. gr. 2.588; hardness $3\frac{1}{2}$. The natural crystals had sp. gr. 2.456 and 2.30, but enclosed impurities; μ 1.508.

The new mineral is thus very similar in its characters to northupite (sp. gr. 2.38; μ 1.514), and the apparent isomorphism of a sulphate with a chloride is only to be explained by the “mass effect” of the complex molecule (compare Penfield and Foote, Abstr., 1899, ii, 305; Hillebrand and Penfield, Abstr., 1902, ii, 667). The facts that *tychite* takes so long to form and that it is not decomposed by boiling water suggest that the molecule is one of considerable stability. Structural formulæ are given showing the relation between *tychite* and northupite.

An attempt to prepare crystals containing both sulphate and chloride was unsuccessful, the resulting octahedral crystals having the composition $2\text{MgCO}_3, 2\text{Na}_2\text{CO}_3, \text{Na}_2\text{CO}_3$.

L. J. S.

Purpurite, a New Mineral. L. C. GRATON and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1905, [iv], 20, 146—151).—This mineral is found as small, irregular masses in pegmatite-veins and in the surrounding schists at the Faires tin mine, King's Mountain, Gaston Co., North Carolina, where it is associated with cassiterite and lithium minerals (lepidolite, spodumene, and tourmaline). Its most striking feature is its purple or dark red colour, and it has a peculiar satiny lustre or sheen; the powder and streak have a decided purple or deep rose colour. It possesses distinct cleavages, and from its optical characters appears to be orthorhombic. In very thin sections it is transparent and pleochroic. Hardness, $4\frac{1}{4}$; sp. gr., 3.15. The following analysis gives the formula $\text{Fe}_2\text{O}_3, 2\text{Mn}_2\text{O}_3, 3\text{P}_2\text{O}_5, 3\text{H}_2\text{O}$, or, if manganic and ferric oxides are isomorphous, $(\text{Mn}, \text{Fe})\text{PO}_4, \text{H}_2\text{O}$. The water is given off at a low temperature, 3.31 per cent, being lost at 105° . The mineral is readily soluble in hydrochloric acid with evolution of chlorine. Several mineral arsenates containing manganic oxide are known, but a manganic phosphate has not been previously described.

Fe_2O_3 .	Mn_2O_3 .	P_2O_5 .	H_2O .	CaO .	Na_2O .	Li_2O .	Insol.	Total.
15.89	29.25	47.30	5.26	1.48	0.84	trace	0.52	100.54

Purpurite has been produced by the alteration of a yellowish-brown mineral with which it is found in association, and which is probably lithiophilite (LiMnPO_4). It is itself always surrounded and penetrated by a black, pitchy material, which under the microscope appears to be a definite mineral; this alteration product of purpurite contains iron, manganese, phosphoric acid, and water, but as yet has not been completely determined.

Purpurite with the same characteristic purple colour has also been found in the lithium-bearing pegmatite-veins at Pala, in San Diego Co., California, where it has resulted by the alteration of triphylite, $(\text{Fe}, \text{Mn})\text{LiPO}_4$.
L. J. S.

Mineralogical Notes. [Gyrolite, Prehnite, Anhydrite, Bournonite, Glaucodote.] WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Surv.*, 1905, 262, 121—144).—*Gyrolite*.—This occurs as spherical, platy, or plumose aggregates filling veins in a basaltic rock at Fort Point, San Francisco, California. The colour is white and the lustre pearly. It is sometimes associated with apophyllite, but there is nothing to suggest that the gyrolite has been derived from the apophyllite. Cleavage flakes show the emergence of a negative bisectrix with $2E = 0-25^\circ$. Gyrolite is closely related to heulandite, and is possibly monoclinic. Analysis I agrees with Clarke's formula, $5\text{H}_2\text{O}, 4\text{CaO}, 6\text{SiO}_2$. Analysis II is of *prehnite* from Lower California.

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	Na_2O .	K_2O .	H_2O .	Total.	Sp. gr.
I. 53.47	0.22	trace	32.00	trace	1.25	trace	13.21	100.15	2.39
II. 43.48	24.52	0.34	27.19	—	—	—	4.49	100.02	2.90

Anhydrite.—Small crystals have been found in Texas, but the exact locality is not known. Analysis gave: CaO , 41.01; SO_3 , 58.87; loss on ignition, 0.22; insoluble, 0.06; total 100.16.

Bournonite.—Analysis III is of massive material from Bogg's mine, in Yavapai Co., Arizona.

Glaucodote.—A sample of cobalt ore from Sumpter, Oregon, consists of massive and imperfectly crystallised glaucodote and pyrites in a dark silicate rock. A small crystal was determined to be orthorhombic. Analysis IV corresponds with the formula $\text{Co}_3\text{Fe}_2(\text{AsS})_5$.

	S.	As.	Sb.	Pb.	Cu.	Fe.	Co.	Zn.	Mn.	Insol.	Total.
III.	20.04	2.81	18.99	40.21	15.12	0.35	—	0.35	trace	1.67	99.54
IV.	18.46	39.84	—	—	—	12.45	20.23	—	—	9.38	100.36

The chemical (Abstr., 1904, ii, 348) and crystallographic characters of several other minerals from American localities are given.

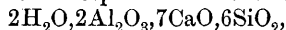
L. J. S.

Californite. FRANK W. CLARKE and GEORGE STEIGER (*Bull. U.S. Geol. Surv.*, 1905, No. 262, 72—74).—A compact variety of idocrase resembling jade in appearance, from Siskiyou Co., California, has been described by G. F. Kunz under the name californite (Abstr., 1904, ii, 50). Similar material (anal. I) is found also in Fresno Co., California: with it is associated a compact white mineral, somewhat resembling chalcedony in appearance, which is optically isotropic and is proved by analysis II to be garnet.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .	CaO .
I.	36.55	18.89	0.74	0.74	nil	2.33	35.97
II.	38.59	22.24	0.45	0.36	0.10	0.64	35.97

	H_2O (105°).	H_2O (>105°).	CO_2 .	F.	Total.	Sp. gr.
I.	0.58	3.42	0.91	0.13	100.26	3.359
II.	0.31	0.80	0.39	0.17	100.02	3.586

Analysis I of idocrase corresponds with the formula



or, rejecting part of the water, $\text{Al}_2\text{Ca}_7(\text{SiO}_4)_6(\text{Al}\cdot\text{OH})_2$. A study of previously published analyses of idocrase suggests that the variations in composition of this species may be explained by mixtures of the following molecules, the first and third of which usually predominate: $\text{Al}_2\text{Ca}_7(\text{SiO}_4)_6(\text{Al}\cdot\text{OH})_2$; $\text{Al}_2\text{Ca}_7(\text{SiO}_4)_6(\text{AlO}_2\text{H}_2)_4$; $\text{Al}_2\text{Ca}_7(\text{SiO}_4)_6\text{H}_4$; $\text{Al}_2\text{Ca}_7(\text{SiO}_4)_6\text{Ca}_2$. About one-seventh of the calcium is replaced by magnesium, and in the variety wiluite the group (BOH) probably occurs. Idocrase is a basic orthosilicate belonging to the same group as garnet, epidote, and the scapolites; they are all products of contact-metamorphism and yield the same alteration-products. L. J. S.

Causes of Variegation in Keuper Marls. GERALD T. MOODY (*Quart. J. Geol. Soc.*, 1905, 61, 431—437).—Several analyses are given of the red and of the greenish-grey portions, each selected from the same hand-specimens, of Keuper Marls from the West of England. The following (I, green portion; II, red portion), of material from Wainlode Cliff on the Severn, may be quoted as examples:

	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	CO ₂ .	H ₂ O (100°).	C (organic).	SiO ₂ .	Al ₂ O ₃ .	TiO ₂ .	Alk., comb. H ₂ O, undet.
I.	0·87	0·96	7·37	6·10	13·01	3·01	0·092	50·84	13·12	0·42	4·208
II.	3·80	0·91	5·18	5·42	10·21	3·72	0·106	50·91	12·98	0·33	4·208
III.	4·96	0·61	4·92	4·77	9·61	75·13					6·434

As shown by these analyses, as well as by all the others, the red portion contains more ferric oxide and less calcium and magnesium carbonates than the green portion of the same hand-specimen. It was found that from the red portion the ferric oxide cannot be extracted by dilute acid so long as carbonates are present. The green portion cannot therefore have been produced by the bleaching of the red portion. Neither can the red portion have been produced by the oxidation of ferrous iron in the green portion, since this constituent is present in both portions in about the same amounts, existing probably as a ferrous silicate. When, however, a chalybeate water permeates a calcareous rock, iron is deposited as ferrous carbonate, and an equivalent amount of magnesium and calcium passes into solution; on subsequent exposure to air, the ferrous carbonate is oxidised to ferric oxide. By passing an artificial chalybeate water (ferrous hydrogen carbonate solution) over the finely-powdered green marl for several hours and afterwards drying in contact with the air, a product was obtained which closely resembled the natural red marl both in colour and composition (anal. III). It is therefore concluded that the variegation of the Keuper Marls and of other calcareous rocks has been brought about by the percolation of chalybeate water through the more porous portions of the lighter coloured mass.

L. J. S.

The Rodeo Meteorite. OLIVER C. FARRINGTON (*Field Columbian Museum, Geol. Ser.*, 1905, 3, 1—6).—This mass of iron, weighing 97 pounds, was found in 1852 near Rodeo, in the State of Durango, Mexico. It is an octahedrite of medium coarseness, with large inclusions of schreibersite and some graphite, but no troilite. Analysis by H. W. Nichols gave:

Fe.	Ni.	Co.	Cu.	P.	S.	C.	Total.
89·84	8·79	0·28	0·07	0·80	0·02	0·09	99·89

L. J. S.

The Shelburne Meteorite. LEONARD H. BORGSTRÖM (*Trans. R. Astron. Soc. Canada*, 1905, [for 1904], 69—94).—This meteorite was observed to fall on August 13, 1904, near the village of Shelburne, Grey Co., Ontario; two masses, weighing 12·6 and 6 kilos., were found. They penetrated the soil to depths of 0·55 and 0·40 metre respectively, and from this it is calculated that their velocity was 172 and 165 metres per second respectively; from other data (air resistance and gravity) the velocities are calculated as 177 and 157 metres per second respectively. The structure of the stones is chondritic. Sp. gr. 3·499. By microscopical examination, four different zones are distinguished in the crust: (1) the outer black crust of varying thickness,

but averaging 0.1 mm.; (2) a layer of brown glass, 0.02 to 0.03 mm. thick; (3) a colourless layer, consisting of grains of silicates, 0.02 to 0.10 mm. thick; (4) a layer consisting of silicates with many opaque particles, 0.1 to 0.4 mm. thick. From analyses of the metallic portion and of the soluble and insoluble silicates, the following general composition of the stone is obtained:

SiO ₂ .	Fe.	Ni.	Co.	FeO.	MnO.	Al ₂ O ₃ .	Cr ₂ O ₃ .
39.19	10.70	0.78	0.04	15.16	0.12	2.15	0.62
CaO.	MgO.	K ₂ O.	Na ₂ O.	S.	P.	Total.	
1.75	26.24	0.22	0.73	1.61	0.06	99.37	

This corresponds with the mineralogical composition: nickel-iron, 8.5; troilite, 4.5; chromite, 0.8; schreibersite, 0.4; olivine, 45.0; enstatite, 27.8; aluminium silicate (maskelynite?), 13.0 per cent.

The metallic portion contains: Fe, 91.08; Ni, 8.44; Co, 0.48 per cent. The olivine is an iron-rich variety, approaching fayalite, and has the following composition:

SiO ₂ .	FeO.	MgO.	CaO.	Al ₂ O ₃ .	Cr ₂ O ₃ .
36.41	23.22	39.66	0.33	0.31	0.07

L. J. S.

Mineral Waters of Fumade. A. ASTRUC and J. DELORME (*Bull. Soc. chim.*, 1905, [iii], 33, 998—1000).—A list is given of the chief mineral springs of Fumade (Gard), of which the most important are the Romaine spring and the Zoé spring, analyses of which are given.
G. Y.

Physiological Chemistry.

Permeability of the Membrane of Fundulus Eggs. ORVILLE H. BROWN (*Amer. J. Physiol.*, 1905, 14, 354—358).—The membrane of the eggs of *Fundulus heteroclitus* is impermeable to salts and water during the first six or eight hours: that is, eggs placed in distilled water do not lose their salts during that period. It becomes permeable after about eighteen or twenty hours, and is equally so to water and salts. W. D. H.

Chemistry of Fishes' Eggs. OLOF HAMMARSTEN (*Chem. Centr.*, 1905, ii, 342; from *Skand. Archiv Physiol.*, 17, 113—132).—Ripe and unripe eggs of the perch were examined. The proteid is mainly a vitellin-like nucleo-albumin, which does not yield purine derivatives. Mucin is also present, and methods for the separation of the two are given.

The shell of the ripe eggs consists mainly of mucinogen and a little mucin. In the unripe eggs, both are present in only small amount. W. D. H.

Response of the Developing Retina to Light and Radium. THOMAS H. MILROY (*J. Physiol.*, 1905, 33, 69—76).—Up to the fifteenth day of incubation, the chick's retina shows no signs of response to light, such as are observed in the fully-developed eye. Beyond this time, the pigment cells respond to light by throwing out processes which contain pigment, and which clasp the ends of the young rods and cones. There is also a contraction of the inner segments of the rods and cones. As development proceeds, the responses become more distinct, and take place even when light reaches the eye after filtration through the shell. The effects of monochromatic and white light are the same. There is no delay in development in the case of embryos developed in the light. The intraocular fluorescence produced by radium is not sufficient to evoke such responses, but the pigment is scattered through the cell-bodies and driven backwards into the surrounding tissues. Radium emanations gradually produce a disintegration of all the retinal elements, starting with those in front.

W. D. H.

Gas Exchange in Some Lower Animals and its Dependence on Partial Pressure of Oxygen. TORSTEN THUNBERG (*Chem. Centr.*, 1905, ii, 345; from *Skand. Arch. Physiol.*, 17, i, 133—195).—The investigations were made in certain molluscs and worms. In pure oxygen, the uptake of that gas is much increased. Differences between the different animals are noted in detail.

W. D. H.

Estimation of the Gas set free in the Body after Rapid Decompression from High Atmospheric Pressures. C. HAM and LEONARD E. HILL (*Proc. Physiol. Soc.*, 1905, vi—vii; *J. Physiol.*, 33).—The gases from the bodies of rats subjected to this treatment were analysed. Most was found in the peritoneal cavity. The total gas varied in three experiments from 9 to 13 c.c. It contained from 6·7 to 16 per cent. of carbon dioxide, and from 2 to 8·7 per cent. of oxygen, the rest being nitrogen.

W. D. H.

Oxygen Inhalation as a means of preventing Caisson and Divers' Sickness. C. HAM and LEONARD E. HILL (*Proc. Physiol. Soc.*, 1905, vii—viii; *J. Physiol.*, 33).—H. von Schrötter has suggested the use of oxygen inhalation (to wash out the nitrogen) for five minutes previous to decompression of caisson-workers. The method is theoretically correct, and in animals is efficacious in preventing death from embolism. It, however, is unsafe to use the method at pressures of 50 lbs. and upwards on account of the danger of oxygen-poisoning.

W. D. H.

Effect of Increased Carbon Dioxide Tension, together with Increased Atmospheric Pressure. C. HAM and LEONARD E. HILL (*Proc. Physiol. Soc.*, 1905, v—vi; *J. Physiol.*, 33).—The conclusion is drawn that increased pulmonary ventilation depends on the carbon dioxide tension. As others have shown, oxygen tensions of less than 10 per cent. atmosphere alter the respiration, but the jerky movements are quite unlike the deep heavings produced by carbon dioxide.

W. D. H.

Effects of High External Temperature on the Body-temperature, Respiration, and Circulation in Man. A. E. BOYCOTT and JOHN S. HALDANE (*Proc. Physiol. Soc.*, 1905, xii; *J. Physiol.*, 33; *J. Hygiene*, 1905, 5, 494—513).—In still air, the body-temperature rises above normal when the wet-bulb thermometer rises over 31° (88° F.), and remains normal whatever the external temperature may be when the wet-bulb thermometer does not rise beyond this point. The greater the rise above 31° , the more rapid the rise of body-temperature. In moving air, the limit is 35° . With rise of body-temperature, a marked fall in the alveolar carbon dioxide pressure is observed, and an increase in the pulse rate.

W. D. H.

Absorption Coefficients of Blood and Blood-plasma for Gases. CHRISTIAN BOHR (*Chem. Centr.*, 1905, ii, 339—340; from *Skand. Archiv Physiol.*, 17, 104—112).—In order to settle the important biological questions relating to the chemical union of carbon dioxide and oxygen in part in blood, blood-plasma, and corpuscles, it is necessary to know Bunsen's absorption coefficients for these media in order to calculate the quantities of these gases which are absorbed in proportion to the pressure. The difficulty of the investigation is increased by the fact that a part of the gas is present in dissociable compounds. Zuntz has estimated the absorption coefficient of gases which do not form compounds with blood constituents, and from these calculates that of oxygen, on the assumption that the proportion between the coefficients for blood and water is constant for all gases.

Whether this is the case has never been investigated. In the present research, the indifferent gas oxygen was used for serum, and hydrogen for the total blood. The fluid was shaken with the gas at constant temperature, and the gas subsequently extracted by the air-pump. The results came out as anticipated with only a small error. The figures obtained and the coefficients reckoned from them are given in tables.

W. D. H.

Composition of the Stroma of the Blood-discs and Hæmolysis. OLINTO PASCUCCI (*Beitr. chem. Physiol. Path.*, 6, 543—551, 552—566).—The observations lend no support to Rollett's idea of a stroma, but rather to its membranous nature; it is a proteid permeable membrane with a large amount of lecithin, cholesterol, and a cerebroside. It has the chemical and physical behaviour of Overton's "lipoid" membranes found in protoplasmic cells. Substances which produce hæmolysis do so by acting on the membrane; this view is supported by numerous experiments on membranes of similar composition.

W. D. H.

Koeppé's Hypothesis of the Nature of the Red Blood Corpuscles. G. GRYNS (*Pflüger's Archiv*, 1905, 109, 289—299. Compare Koeppé, *Abstr.*, 1903, ii, 736; 1904, ii, 650; this vol., ii, 331).—A criticism of Koeppé's view that the red discs are covered with a membrane consisting essentially of fatty materials. The main points are as follows. (1) If the membrane consists of fatty material it would not be moistened by the water, and rupture could not therefore be

due to differences in osmotic pressure. (2) After rupture, the membrane, if of a fatty nature, should be recognisable by its high refractive power. (3) The membrane is not dissolved by alcohol or ether.

The results with regard to centrifugalising are also criticised.

J. J. S.

Glycuronic Acid of Blood. RAPHAEL LÉPINE and BOULUD (*Compt. rend.*, 1905, 141, 453—456. Compare Abstr., 1903, ii, 493, and 1904, ii, 422).—It is improbable that glycuronic acid is formed at the expense of the lævulose, and the small amount of dextrose present in blood is insufficient to account for it. It is probably produced from dextrose obtained from the considerable amount of glucoside nearly always present in blood.

N. H. J. M.

Action of Vaso-dilators. V. E. HENDERSON and OTTO LOEWI (*Chem. Centr.*, 1905, ii, 344; from *Arch. exp. Path. Pharm.*, 53, 56—61).—In vaso-dilatation, not only are the vessels widened in the sense that their total transverse diameter is increased, but also, and probably mainly, by an increase only in the lumen. Hence it is possible for an organ like the kidney to have dilated blood vessels without an increase of volume.

W. D. H.

Invertin in Blood. ERNST WEINLAND (*Zeit. Biol.*, 1905, 47, 279—288).—In the young dog, invertin is only found in the small intestine normally, but after continuous subcutaneous injection of sucrose, it is found also in the blood. If inulin is used instead, no evidence was found of the formation of a ferment able to split it up.

W. D. H.

Anti-precipitins. P. BERMBACH (*Pflüger's Archiv*, 1905, 109, 73—77).—The fact that a serum will prevent the precipitating action of precipitin is not trustworthy evidence of the presence of an anti-precipitin. Certainly, long treatment of an animal (rabbit) with injections of precipitin does not lead to the formation of an anti-substance.

W. D. H.

Chemistry of Digestion. I. E. S. LONDON (*Zeit. physiol. Chem.*, 1905, 45, 381—385).—A preliminary description of the methods of making fistulæ in dogs (in accordance with Pawloff's ideas), by which it is proposed to investigate some of the questions of digestion-chemistry.

W. D. H.

Chemical Mechanism of Gastric Secretion. J. S. EDKINS (*Proc. Roy. Soc.*, 1905, 76 B, 376).—The mechanical and nervous provocation to the secretion of gastric juice must be supplemented by a theory of chemical stimulation, as Bayliss and Starling have shown to be the case in the pancreas. If an extract of the mucous membrane of the fundus of the stomach, made with a 5 per cent. solution of dextrin, is injected into the jugular vein, no secretion of gastric juice follows; the same is true for dextrin by itself. But a dextrin

extract of the pyloric mucous membrane excites a small secretion of the juice. The same is true for extracts made with dextrose or maltose, or peptone, but the positive result with pyloric extracts is more marked. It therefore appears that salivary digestion provides a chemical cause for the secretion of the next juice in order. The term suggested for the active substance is "*gastrin*." It is not destroyed by boiling, and so falls into line with many other "hormones" (Starling's term for these chemical stimuli). W. D. H.

Formation of Hydrochloric Acid in the Stomach. ALFRED BENRATH and FRITZ SACHS (*Pflüger's Archiv*, 1905, 109, 466—472).—Absence of chlorine ions in the food does not prevent formation of hydrochloric acid. Presence of chlorine ions in the food does not necessarily evoke hydrochloric acid formation. Introduction of chlorine-free salt solutions into the stomach does not abolish the acid of the secretion which comes from the blood. The quantity of the acid secreted has no relation to the chlorine administered. The formation of hydrobromic acid after introducing sodium bromide into the stomach is also explained by absorption into the blood and subsequent glandular activity. The impermeability of the stomach to chlorine ions is not proved. These facts all tell against Koppe's theory. W. D. H.

Antipepsin. OSW. SCHWARZ (*Beitr. chem. Physiol. Path.*, 1905, 6, 524—542).—The existence of substances antagonistic to ferments has been abundantly proved by numerous researches, references to which are given. In some cases, the appearance of the anti-substance is provoked by injection of the ferment, as in researches on immunity; in other cases, the anti-substance is normally present, and in the case of the stomach the existence of antipepsin explains why the stomach does not digest itself. It has been shown that antitrypsin resists the action of heat (Pollak); the same is true for the substance which is inhibitory to peptic activity. It is precipitable by alcohol. It is present in preparations of pepsin, and the inhibitory influence, measured by experiments with Mett's tubes, is proportional to the amount of boiled pepsin solution added. Albumoses act inhibitingly in a similar way, but the boiled and filtered solutions of pepsin which are inhibitory give no biuret reaction. Possibly the biuret reaction is not a sufficiently sensitive one to detect the small amount of substance present. Danilewsky and others deny the proteid nature of antipepsin. The question arises whether the latter substance is preformed or an artifact produced by boiling the pepsin solution. The answer given is that the former alternative is correct. If proteid is soaked in pepsin solution, the pepsin is removed by absorption, and the residual fluid contains no pepsin, but antipepsin is present before and after boiling it. The antipepsin does not destroy pepsin, but forms with it an inactive "neutral" complex. W. D. H.

A Fat-hydrolysing Ferment from the Mucous Membrane of the Stomach. ALBERT FROMME (*Beitr. chem. Physiol. Path.*, 1905, 7, 51—76. Compare Volhard, *Abstr.*, 1901, ii, 518; 1903, ii, 120, 494).—The author confirms the presence of a fat-hydrolysing

ferment (steapsin) in the mucous membrane of the stomach. Similar ferments may be obtained from dogs and pigs, either from the dry material or by glycerol extraction. The pylorus end of the stomach does not contain such a ferment. The ferment from pigs behaves differently from the human ferment. Its action is accelerated by alkali and retarded by acid. The ferment obtained from dog's stomach by glycerol extraction is not affected by acids, but is sensitive to alkalis, and thus resembles the human steapsin. J. J. S.

Extent to which Fats are Decomposed in the Stomach. ADOLF ZINSSER (*Beitr. chem. Physiol. Path.*, 1905, 7, 31—50. Compare Fromme, preceding abstract).—When a fat emulsion is introduced into a normal stomach, about 25 per cent. of the fat is hydrolysed at the end of one hour, and in all probability this value obtained experimentally is below the actual value. No direct relationship can be established between the time and degree of hydrolysis.

The hydrolysis is less in cases of hyperacidity, but considerably greater (45 per cent. in one hour) in cases of achylia gastrica. The decomposition is produced by an enzyme which remains behind when the juices are filtered. J. J. S.

Estimation of Parachymosin, and Time Laws of Human Rennin Ferment. GEORG BECKER (*Beitr. chem. Physiol. Path.*, 1905, 7, 89—119. Compare Fuld, Abstr., 1902, ii, 415, 675).—The ordinary time law for coagulation (namely, amount of ferment \times time of coagulation = constant) does not hold good for parachymosin (Bang, Abstr., 1900, ii, 356). The relative falling off in the coagulating action when experiments are conducted for a long time is not due to the liquids necessarily required for dilution. The addition of calcium chloride and acid favours the coagulation, and when added in certain proportions and allowed to react for a short time (five hours), the coagulation approximates to the ordinary time law for calves' rennin.

For the estimation of parachymosin, the simplest method is to determine the amount of juice required to produce the coagulation of 10 c.c. of milk containing 2 per cent. of hydrochloric acid, when the mixture is kept in an ice-chest for thirty minutes and then warmed for five minutes. J. J. S.

Time and Fermentation Laws of Pancreas-steapsin. HANS ENGEL (*Beitr. chem. Physiol. Path.*, 1905, 7, 77—88. Compare Schütz, Abstr., 1885, 1147; Borissow and Linossier, *J. Physiol. Path.*, 1899, 1; Schütz and Huppert, 1900, ii, 553).—The Schütz-Huppert laws, namely, v/\sqrt{ft} = constant, hold good for pancreas-steapsin, and the amount of ferment can be calculated from the equation $x = v^2/ft$, where v = percentage of fat decomposed, f the volume of ferment solution in c.c., and t the time in hours. J. J. S.

End-products of Pancreatic Autolysis. PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1905, 45, 498—499. Compare Abstr., 1903, ii, 670, 737; 1904, ii, 425).—The statement made by Kutscher and Lohmann (this vol., ii, 466) that thymine and uracil are not products

of pancreatic autolysis is incorrect. If sufficient time is allowed to elapse, they are always found by the author's method. W. D. H.

Utilisation of Carbohydrates without Intervention of Alimentary Digestion Processes. LAFAYETTE B. MENDEL and PHILIP H. MITCHELL (*Amer. J. Physiol.*, 1905, 14, 239—247).—There are no profound differences between glycogen and dextrin in their "parenteral" introduction into animals; glycogen is retained rather better. The failure of the organism to retain carbohydrates, which it is not fitted to transform into mono-saccharides by ferment action, is well illustrated by experiments with inulin and isolichenin. The importance of the alimentary digestive changes in the metabolism of carbohydrates stands on a firm footing. W. D. H.

Influence of Movement of the Body on the Digestion and Absorption of Food-stuffs in the Horse. ARTHUR SCHEUNERT (*Pflüger's Archiv*, 1905, 109, 145—198).—Movement during the digestion of food tends to retard the passage of material from the stomach to the intestine, and at the same time increases the percentage of water in the stomach. This is due mainly to the increased secretion of water from the mucous membrane during motion. In spite of the increased percentage of water, movement of the body, even galloping, does not tend to mix the stomach contents.

Motion increases the digestion of carbohydrate and the general secretion of the stomach juices, but at first tends to lessen the digestion of nitrogenous substances and proteids, but later this is also intensified, as is also the absorption of food by the stomach.

The decomposition and absorption in the intestine are only slightly affected by bodily movement.

Most of the experiments were made with relatively old horses, and the results vary somewhat with the individual animals. J. J. S.

Movements of the Surviving Intestine. JOHN N. LANGLEY and RUDOLF MAGNUS (*J. Physiol.*, 1905, 33, 34—51. Compare Magnus, *Abstr.*, 1905, ii, 466).—The experiments of Bayliss and Starling on the dog's intestine are in the main true also for cat and rabbit. Strong and fairly regular contractions can be obtained after section of vagi and superior mesenteric nerves by direct application of 1 per cent. atropine, 0.5 to 3 per cent. strychnine, and 1 to 10 per cent. cocaine. These and the normal contractions are either lessened or abolished by a stimulus applied above the balloon which is inserted for the registration of the movements. Inhibition is usually produced by direct application of sodium chloride solutions. Degenerative section of the nerves does not abolish any of these effects or the inhibition normally produced by adrenaline and by nicotine. W. D. H.

Action of the Mucous Membrane of the Surviving Intestine on Soaps, Fats, and Fatty Acids. OTTO FRANK and ADOLF RITTER (*Zeit. Biol.*, 1905, 47, 251—267).—In order to determine the seat of synthesis of fats from their hydrolytic products formed during digestion, Ewald, and later Hamburger, incubated

finely-divided intestinal mucous membrane with these products, and determined the amount of neutral fat after some hours. Their results were irregular and unconvincing. Moore could not discover any new formation of fat at all. The present experiments, carried out with calf's mucous membrane and various mixtures of soap, fatty acids, and glycerol, confirm Moore's statement. Considerable importance is attributed to the formation of carbon dioxide during digestion, and this substance is believed to be responsible for the liberation of fatty acids from soaps. W. D. H.

Liver Autolysis. JULIUS BAER and ADAM LOEB (*Chem. Centr.*, 1905, ii, 345; from *Arch. exp. Path. Pharm.*, 53, 1—14).—The question investigated is whether the blood contains a true anti-ferment against autolysis. Serum inhibits autolysis of the liver even after it has been heated to 95°. The evidence is therefore against an anti-ferment. Acid added to the serum increases the autolysis; solution of sodium hydrogen carbonate in small quantities acts in the same way. Serum globulin hastens, serum albumin delays it. Boiling destroys the hastening action of the former, but not the inhibiting action of the latter proteid. W. D. H.

[Effect of Feeding with Material Rich in Arginine.] GUSTAV ORGLMEISTER (*Beitr. chem. Physiol. Path.*, 1905, 7, 27—30).—Feeding dogs with material rich in arginine does not appear to increase the amounts of arginine in the various organs, and feeding birds with benzoic acid does not tend to decrease the amounts of arginine to any appreciable extent. J. J. S.

The Nutritive Value of Amino-compounds. BOLESLAUS VON STRUSIEWICZ (*Zeit. Biol.*, 1905, 47, 143—185).—From experiments on sheep, the conclusion is drawn that the metabolic value of amino-compounds is the same as that of proteid. W. D. H.

Metabolic Changes during the Metamorphosis of the Meat-fly (*Calliphora Vomitoria*). ERNST WEINLAND (*Zeit. Biol.*, 1905, 47, 186—231).—In the metamorphosis of the pupa there is at first lessening of respiratory processes; these then remain at a low level, and finally, with the appearance of movements, they are increased and lead to great loss of weight. Combustion of fat is the main source of the carbon dioxide given out; no oxidation of carbohydrate was proved to occur, but there is the formation of a small amount of carbohydrate material (chitin), which is the result of the breakdown of nitrogenous substances. W. D. H.

Folin's Theory of Proteid Metabolism. DIARMID NOËL PATON (*J. Physiol.*, 1905, 33, 1—11. See Folin, Abstr., 1905, ii, 183, 268).—Folin's theory is, on the whole, agreed with, but certain differences of detail are noted; for instance, in the dog, creatinine excretion is not so constant as in man. A doubt is expressed whether any hard and fast line can be drawn between endogenous and exogenous proteid metabolism, and urea may probably be a result of both. Some

of Folin's results may be explained by variations in the activity of the liver, for it is here that urea precursors are transformed into that substance. Of all diets, proteid is the best to stimulate hepatic metabolism, as gauged by the amount of bile secreted. Hence, on a diet poor in proteid it may be sluggish, and therefore fail to convert much of the waste nitrogen into urea, whilst on a diet rich in proteid the conversion will be more complete. The amount of sulphur which is completely oxidised must also depend on hepatic activity.

W. D. H.

Gelatin in Metabolism. MAURICE KAUFFMANN (*Pflüger's Archiv*, 1905, 109, 440—465).—From experiments on two dogs and also on the author, it was determined that the proteid (plasmon) in the diet can be replaced to the extent of one-fifth by gelatin without harm. This can be exceeded and the proteid completely replaced by gelatin if it is mixed with tyrosine, cystine, and tryptophan. Both dogs, however, died.

W. D. H.

Chemical Correlation of the Functions of the Body. ERNEST H. STARLING (*Lancet*, 1905, ii, 501—503, 579—583).—A series of lectures (Croonian lectures, Royal College of Physicians) giving an account of the numerous researches recently carried out by the author and his colleagues on the chemical messengers which bring about correlation of function between different organs of the body. The general name bestowed upon them is *hormone*. Some, like secretin, stimulate increased activity and katabolism, others involve increased assimilation and growth. Under the latter head fall the internal secretions of the thyroid and generative organs. Preliminary experiments indicate that it is an internal secretion of the fœtus which leads to the growth of the mammary gland.

W. D. H.

Occurrence of Lithium in the Human Body. ERICH HERRMANN (*Pflüger's Archiv*, 1905, 109, 26—50).—Lithium appears to be present in practically all the organs of the human body. It is also present in the earlier stages of development (fœtus), where the feeding has been entirely by means of the maternal blood. The lungs appear to be richest in lithium.

The detection of lithium in presence of considerable quantities of phosphates cannot be carried out in the usual manner, and a method is recommended which is based on the fact that lead phosphate is insoluble in acetic acid and lithium acetate is readily soluble in water.

J. J. S.

Conditions for the Formation of Acetone [in the Body]. RICHARD WALDVOGEL (*Beitr. chem. Physiol. Path.*, 1905, 7, 150—151. Compare Satta, this vol., ii, 406).—Polemical.

J. J. S.

Fate of Oil Injected Subcutaneously. YANDELL HENDERSON and EDWARD FRANCIS CROFUTT (*Amer. J. Physiol.*, 1905, 14, 193—202).—Cotton-seed oil injected subcutaneously in dogs is rapidly and widely distributed through the subcutaneous spaces, but it is not transformed

in situ into adipose tissue. The tissues react to its presence as to any non-irritating foreign substance. It does not appear in detectable amounts in blood, lymph, or milk. It is ultimately absorbed and utilised, but the process is so slow that oil injections are practically destitute of nutritive value. W. D. H.

Effect of Dextrose and Certain Salts on the Rate of Transformation of Glycogen into Dextrose. C. HUGH NEILSON and OLIVER P. TERRY (*Amer. J. Physiol.*, 1905, 14, 105—111).—It is suggested that the change of dextrose into glycogen and *vice versa* in the body is due to the reversible action of a single enzyme. The change into sugar is certainly retarded by excess of sugar. Calcium chloride retards, and sodium citrate accelerates, the change. The action of salts is probably one on cell-membranes. W. D. H.

Distribution of Glucothionic Acid in the Animal Organism. JOHN A. MANDEL and PHOEBUS A. LEVENE (*Zeit. physiol. Chem.*, 1905, 45, 386—392. Compare Abstr., 1903, ii, 314).—By the use of Levene's method, glucothionic acid was isolated from mammary gland, kidney, liver, and pancreas. W. D. H.

Cystine. EMIL FISCHER and UMETARŌ SUZUKI (*Zeit. physiol. Chem.*, 1905, 45, 405—411. Compare Abstr., 1905, i, 121).—By dissolving cystine in dry methyl alcohol and allowing a stream of dry hydrogen chloride to pass through it, a cystine dimethyl ester hydrochloride was obtained. This forms crystalline salts which serve to identify cystine. No differences could be detected between cystine prepared from calculi and that prepared from horse-hair. Neuberg and Mayer's contrary result is probably explicable by admixture with tyrosine. W. D. H.

The Silver Reaction in Animal and Vegetable Tissues. ARCHIBALD B. MACALLUM (*Proc. Roy. Soc.*, 1905, 76 B, 217—229).—One view, which seeks to explain the well-known reduction stain with silver nitrate so much used in histology, states that a silver-proteid compound in the cementing material is the substance which is acted on by light. But proteids freed from salts, or tissues washed free from salts, no longer give the reaction. Taurine and creatine out of a large number of organic substances examined give the reaction, but these exceptions may be eliminated. The conclusion is drawn that the halogen in haloid form is the cause of the reaction. Intercellular material is specially rich in chlorides, and the reaction may be used to determine the distribution of chlorides in histological specimens. The normal nuclei of animal and vegetable cells do not contain chlorides at all. W. D. H.

The Masking of Ionic Effects by Organic Substances. PERCY GOLDTHWAIT STILES and WILLIAM HERBERT BEERS (*Amer. J. Physiol.*, 1905, 14, 133—137).—Well-known ionic effects on muscle are masked by the presence of organic substances with large molecules; this is regarded as an indication of combination. W. D. H.

Supposed Equivalence of Sodium and Lithium Ions in Skeletal Muscle. CARL SPENCER MILLIKEN and PERCY GOLDTHWAIT STILES (*Amer. J. Physiol.*, 1905, 14, 359—365).—The ions sodium and lithium are very similar physically, but are not equivalent physiologically. There is, however, no foreign ion which is so slow to make a noteworthy change in skeletal muscle as lithium, but when much of the normal sodium is replaced by lithium, a characteristic fall in irritability follows. No irreparable harm results, for by a reversal of treatment the muscle can be restored. The harmlessness of lithium does not obtain for all tissues. W. D. H.

Paths of Absorption from the Liver. LAFAYETTE B. MENDEL and FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1905, 14, 252—258).—Absorption of injected materials (milk, &c.) from lymph spaces is not different in the liver from what it is in serous cavities and other lymph spaces. W. D. H.

Physiology of Molluscs. II. Inorganic Constituents of the Liver of *Sycotypus*. LAFAYETTE B. MENDEL and HAROLD C. BRADLEY (*Amer. J. Physiol.*, 1905, 14, 313—327).—Copper, zinc, iron, calcium, magnesium, and phosphorus are normal constituents of the liver of *Sycotypus*. Copper comprises 8 per cent. of the total ash, or 1.2 per cent. of the dry tissue; the corresponding numbers for zinc are 15 and 1.7; both are present in cells and the connective tissue, but the most copper is in the green pigment cells. Both are derived from the food, and are stored in the liver for purposes of blood formation; a respiratory proteid peculiar to this animal occurs in the blood and contains both metals. W. D. H.

The Tauro-choleic Acid of Ox Bile. ALF. GULLBRING (*Zeit. physiol. Chem.*, 1905, 45, 448—458).—Glycocholic and taurocholic acids were found in ox bile by Strecker and prepared in a state of purity by Hammarsten; glycocholeic acid was isolated by Wahlgren; the present investigation is a search for the fourth member of the group, namely, taurocholeic acid. It was found present in small quantities, but was not obtained in crystalline form. W. D. H.

Presence of Bile Pigments in Leeches. CAMILLE SPIESS (*Compt. rend.*, 1905, 141, 333—335).—The product of secretion of the peritoneal cells contains one of the specific principles of the bile, elaborated by the hepatic cells of higher animals.

The peritoneal cells of leeches accumulate a pigment analogous to, if not identical with, the bile pigments of the vertebrates.

N. H. J. M.

Gaseous Metabolism of the Kidney. JOSEPH BARCROFT and T. GREGOR BRODIE (*J. Physiol.*, 1905, 33, 52—68. Compare this vol., ii, 99).—The diuresis produced by urea and sodium sulphate is accompanied by a large increase of the oxygen absorbed by the kidney. This is also the case in phloridzin diabetes. There is not always a simultaneous increase in the carbon dioxide leaving the organ.

The work of concentration, as calculated from the freezing points of the blood and urine, accounts for only a small fraction of the whole energy transformed by the kidney: the two quantities have no fixed relation to one another. In so far as urine of the same freezing point as the serum would represent Ludwig's glomerular filtrate, the experiments lend no support to his theory, for the source of energy for the production of such urine should be the heart and not the kidney; yet it is in these circumstances that the kidney is most active. Diuresis is not always accompanied by increased blood-flow; when it is, the former outlasts the latter. Over a large number of experiments there is an approximate equality between the volumes of oxygen absorbed and the carbon dioxide excreted by the kidney. This suggests, though it does not exactly prove, that the substance of the kidney is completely broken down in the organ itself. In some cases, urine of less molecular concentration than the serum was obtained; the divergence being greatest when the flow of urine has been most rapid.

W. D. H.

Effect of Hypnotics and Anti-pyretics on the Rate of Catalysis of Hydrogen Dioxide by Kidney Extract. C. HUGH NEILSON and OLIVER P. TERRY (*Amer. J. Physiol.*, 1905, 14, 248—251).—Hypnotics have a sedative influence on ferment action, and various drugs of this class were found to retard the catalytic action of kidney extract. Antipyrin was the only anti-pyretic investigated, as it is one of few sufficiently soluble for such experiments. It has the opposite effect.

W. D. H.

Variations in the Amount of Casein contained in Human Milk. GUSTAVE PATEIN and L. DAVAL (*J. Pharm. Chim.*, 1905, 22, 193—200).—The results of 16 analyses show that, one month after delivery, human milk contains on the average 1.0 per cent. of casein, and that the variation in the amount is within narrow limits. The average amount found in 12 analyses of the milk of a woman, 4 to 10 days after delivery, was 1.77 per cent. In estimating casein in milk, it is of great importance not to add too little or too much acetic acid; in the first case, the casein is not completely precipitated, and in the second it is re-dissolved.

W. P. S.

Composition of Abnormal Milk and Ash Constituents. SAGORO HASHIMOTO (*J. Sapporo Agric. Coll.*, 1903, 2, 1—14).—The milk was partly curdled and clotted and partly viscous and was strongly alkaline. When examined microscopically, it was found to contain colostrum and blood corpuscles and fragments of tissue. It had a red colour, due no doubt to the presence of blood, since no chromogenic microbes could be detected.

As regards the composition of the milk, the percentages of dry matter, fat, and lactose were found to be very low (especially the fat and lactose); the proteids were high, whilst the total ash was quite normal. The conclusion is drawn that the excess of proteids represents the amounts which, under normal conditions would be utilised for the production of fat and lactose.

The composition of the ash was as follows :

K ₂ O.	Na ₂ O.	CaO.	MgO	Fe ₂ O ₃	P ₂ O ₅ .	SO ₃ .	Cl.
8.96	36.54	7.44	1.74	0.21	17.38	1.34	33.63

The results show that the ash consists largely of sodium chloride and that the amounts of potassium and phosphoric acid are very low. The low percentage of iron indicates that no great amount of blood can be present in the milk. It is probable that a considerable quantity of blood serum had passed into the milk glands.

The milk was from a Dutch cow which had recently calved after an interval of six years since the last calf. N. H. J. M.

Origin of Lactose. Effects of Injections of Dextrose during Lactation. CH. PORCHER (*Compt. rend.*, 1905, 141, 467—469. Compare this vol., ii, 600).—Injection of dextrose gives rise to lactosuria unless the amount is excessive, in which case glycosuria results. The same amount of dextrose which produces lactosuria when the mammary glands are in full activity may produce glycosuria when the glands are less active. N. H. J. M.

Physiology of the Kidneys. III. Mechanism of Caffeine Diuresis. OTTO LOEWI, W. M. FLETCHER, and V. E. HENDERSON (*Chem. Centr.*, 1905, ii, 343; from *Arch. exp. Path. Pharm.*, 53, 15—32).—Caffeine is not a vaso-constrictor; it dilates the kidney vessels, but not those of other organs. The cause of diuresis is accelerated blood-flow. The effect is one directly in the vessel walls and occurs after the nerves have been cut and degenerated. The increased action of caffeine in nephritis fits in with Traube and Cohnheim's theory of that disease. W. D. H.

Physiology of the Kidney. IV. Mechanism of Salt Diuresis. OTTO LOEWI and NATHANIEL H. ALCOCK (*Chem. Centr.*, 1905, ii, 343; from *Arch. exp. Path. Pharm.*, 53, 33—48).—After saline injections, the more watery condition of the blood is the cause of the dilatation of the blood vessels and of diuresis. If the vessels are fatigued by caffeine, salt again causes them to dilate. W. D. H.

Physiology of the Kidneys. V. Mechanism of Urea Diuresis. V. E. HENDERSON and OTTO LOEWI (*Chem. Centr.*, 1905, ii, 343—344; from *Arch. exp. Path. Pharm.*, 53, 49—55).—Here also diuresis is attributed to hydræmia. The paper concludes with a summary of the modes of action of diuretics. W. D. H.

A New Compound of Sulphur in Dogs' Urine. CARL NEUBERG and GROSSER (*Chem. Centr.*, 1905, ii, 835—836; from *Centr. Physiol.*, 19, 316).—Some years ago J. Abel found that on heating dogs' urine with alkali, an alkyl sulphide, probably ethyl sulphide, was split off from an unknown precursor. The latter is of basic nature and can be precipitated from the urine by phosphotungstic acid and isolated from the precipitate by mineral acid and potassium bismuth iodide. The

base is methyl diethylsulphinium hydroxide, $\text{SMeEt}_2\cdot\text{OH}$. The origin of the base appears to be putrefaction of cystine, which leads to the formation of ethyl sulphide, this being subsequently methylated.

W. D. H.

Cause of the Oxidising Action of Urine. P. SCHURHOFF (*Pflüger's Archiv*, 1905, 109, 83—94. Compare Bertram, this vol., ii, 468).—The oxidising power of urine may be estimated by the following process. The urine, after complete removal of dissolved oxygen, is mixed with 10 c.c. of a sodium hyposulphite solution and the mixture titrated with indigo-carmin solution, a further 10 c.c. of the hyposulphite solution is added, and the titration repeated. The difference between the two readings gives the vol. of standard hyposulphite oxidised by the urine. The hyposulphite must be carefully protected from atmospheric oxygen. The oxidising action is shown to be due to nitrates in the presence of acid phosphates, and only to a slight extent to hydrogen peroxide. The oxidising action can be followed qualitatively by means of ferrous salts without the addition of indigo.

J. J. S.

Excretion of Nitrogen in the White Rat. SHINKISHI HATAI (*Amer. J. Physiol.*, 1905, 14, 120—132).—Estimations of the nitrogen excreted by white rats of different ages and weights are given. The following formula gives accurate results: $\log N = \frac{233 + (3 \times \log B.W.)}{4}$,

where N is total nitrogen in milligrams per diem and B.W. body weight in grams.

W. D. H.

Excretion of Ammonia by the Larvæ of Calliphora. ERNST WEINLAND (*Zeit. Biol.*, 1905, 47, 232—250).—The production of ammonia is a marked feature of the growth of the fly-larvæ. An amino-substance is also formed, the nature of which is uncertain. During the subsequent metamorphosis, ammonia formation ceases. No uric acid was detected until later stages were reached. The relation of these chemical processes to the histolysis which occurs in some of the tissues of the imago is discussed.

W. D. H.

Scatole. CH. PORCHER and CH. HERVIEUX (*Zeit. physiol. Chem.*, 1905, 45, 486—497. Compare Abstr., 1905, ii, 187).—If indole is given to an animal it is excreted as indican. It has been held that scatole loses its methyl group and is similarly excreted. As normal urines always contain indican, a bread and milk diet was given. If scatole is given subcutaneously, it passes out as a chromogen, which, on the addition of strong hydrochloric acid, yields a red pigment (scatole-red); this is soluble in amyl alcohol, but not in ether or chloroform. Urine never contains free scatole. Alkalis or reducing agents remove the colour from scatole-red; its spectrum is identical with that of urorosein. In the organism, scatole does not lose its methyl group, and no indican appears in the urine. The chromogen is found in the urine of domestic animals, especially in the ruminants; its occurrence is probably of diagnostic value in disease.

W. D. H.

Hydrochloric Acid in the Gastric Juice in Cancer. BENJAMIN MOORE (*Proc. Roy. Soc.*, 1905, 76 B, 138—159).—It is well known that the amount of the acid in gastric juice is lessened or abolished in malignant disease of the stomach. It is now shown that the same is true for cancer of other organs also. This is due to diminished concentration of hydrogen ions in the blood-plasma. The problem of how to maintain it against the competition of the body cells is for the future, for administration of acid below the limits of acid intoxication only calls for protective ammonia production from the oxidation of proteids. W. D. H.

Composition of Blood in Cases of Tuberculosis Pulmonum, Carcinoma Ventriculi, Diabetes Mellitus, Saturnismus Chronicus, and Typhus Abdominalis. Clinical Method for Determining the Plasma Conditions in the Blood in Erythema. Capillary Pyknometer. FRANZ ERBEN (*Chem. Centr.*, 1905, ii, 783—784).—Results of analyses of blood (proteids, fat, lecithin, cholesterol, and ash constituents) in connection with the various diseases, and the conclusions drawn from them, are given in the original paper (Vienna and Leipzig, 1905). N. H. J. M.

Excretion of Leucine and Tyrosine in a Case of Cystinuria. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1905, 45, 468—472).—Both leucine and tyrosine were found in the urine in a case of cystinuria (a disorder of intermediary metabolism). Future research will indicate whether or not the excretion of these and other amino-acids is a constant feature of the disease. Tyrosine was also found in the urine of an old woman suffering from jaundice. W. D. H.

Cystinuria. EYVIND BÖDTKER (*Zeit. physiol. Chem.*, 1905, 45, 393—404).—Two cases of cystinuria are described in which cadaverine and putrescine were found in the urine. A review of the literature of the subject is given. W. D. H.

Feeding on Mono-amino-acids in Cystinuria. CHARLES E. SIMON (*Zeit. physiol. Chem.*, 1905, 45, 357—358).—A case of cystinuria is recorded in which no diamines were excreted. After the administration of four to five grams of tyrosine, none could be detected in the urine during the next thirty-six hours. W. D. H.

Production and Inhibition of Glycosuria in Rabbits by Salts. MARTIN H. FISCHER (*Pflüger's Archiv*, 1905, 109, 1—25. Compare this vol., ii, 103, and Brown, *Abstr.*, 1904, ii, 273).—The injection of *N*/6 solutions of sodium chloride, bromide, iodide, or nitrate into the veins of the ears of rabbits produces diuresis and glycosuria. Less concentrated solutions intensify renal activity, but produce little or no glycosuria, and the addition of calcium chloride to the sodium salts inhibits the latter phenomenon. Rabbits differ in the readiness with which glycosuria can be produced or inhibited by the

salts, but there is a definite "latent time" before the specific action of the salt is apparent.

The point of activity of all the salts appears to be the *medulla oblongata*.

Lithium, potassium, and strontium chlorides can also produce glycosuria when injected near to the centre of activity, ammonium chloride is without action, and calcium or magnesium chloride produces death.

The action of the salt solutions is not purely osmotic, since solutions of glycerol, carbamide, or ethyl alcohol of the same osmotic concentration do not produce glycosuria.

J. J. S.

Gout. HEINRICH KIONKA (*Chem. Centr.*, 1905, ii, 847—848; from *Zeit. exp. Path. Ther.*, 2, 1—9, 9—17, 17—25; ERNST FREY, *ibid.*, 848—849; from *ibid.*, 26—36, 36—45).—On an exclusively flesh diet, hens and other animals develop typical gout. A functional disturbance of liver (failure of urea-forming ferments) and kidneys is an important factor in its causation. Remedies fall into three groups: (1) pain sedatives and purgatives, (2) solvents of uric acid such as piperazine, and (3) specifics such as colchicine and salicylic compounds; the latter act as cholagogues. Glycine is recommended in combination with lithium as likely to form a soluble compound with uric acid.

Frey disputes some of Kionka's views, and regards the giving of glycine as the establishment of a "vicious circle." Glycine and urea hasten the precipitation of neutral urates by addition of sodium hydrogen carbonate, the former because it dissociates hydrogen ions, the latter on account of its basic nature.

W. D. H.

Digestive Leucocytosis. II. The Source of the Leucocytes. ALEXANDER GOODALL and DIARMID NOËL PATON (*J. Physiol.*, 1905, 33, 20—33. Compare Abstr., 1903, ii, 669).—The bone-marrow is probably the sole source, and is certainly the only important source, of the cells which constitute digestive leucocytosis.

W. D. H.

Nephritis. FRANZ ERBEN (*Chem. Centr.*, 1905, ii, 784; from *Zeit. klin. Med.*, 50).—The chief alteration in the blood in chronic parenchymatose nephritis is the diminution of the albumin and the increase of globulin. The deficient albumin of the cells, due to the poverty of the blood, resulting from the elimination of albumin in the urine, may be considered as the cause of hypertrophy of the heart. The globulin of nephritis urine is, at least in part, normal serum-globulin.

N. H. J. M.

Chemistry of Malignant Growths. IV. The Pentose content of Tumours. S. P. BEEBE and PHILIP SHAFFER (*Amer. J. Physiol.*, 1905, 14, 231—238).—In cancer of the breast, the amount of pentose is usually higher than in normal breast tissue, and is sometimes extremely high in chronic scirrhus where the nuclear proliferation is not a marked feature.

In the tumours of the liver examined, the amount of pentose does not markedly differ from that found in the normal organ; the pentose-

content of normal tissues varies a good deal. Many more observations are necessary before any theory on the relation of cancer and pentose can be considered satisfactory.

W. D. H.

Potassium and Calcium in Mouse Tumours. GEORGE H. A. CLOWES and W. S. FRISBIE (*Amer. J. Physiol.*, 1905, 14, 173—192).—In adeno-sarcomata of mice, there is a high percentage of potassium and little or no calcium when the tumours are rapidly growing; but in old, slowly growing tumours the reverse obtains.

W. D. H.

Studies on Magnesium Salts. I. Anæsthesia by Subcutaneous Injections. S. J. MELTZER and JOHN AUER (*Amer. J. Physiol.*, 1905, 14, 366—388).—In cats, dogs, frogs and other animals, a certain dose of magnesium sulphate or chloride administered subcutaneously will produce a deep and long-lasting anæsthesia with relaxation of the voluntary muscles and abolition of some of the less important reflex actions. A larger dose leads to death without any symptoms of excitation. No purgative effects were noted. The fall of blood pressure is unimportant. In dogs, local abscesses occurred at the seat of injection, but these healed rapidly.

W. D. H.

Pharmacology of Ammonium Bases. HERM. HILDEBRANDT (*Chem. Centr.*, 1905, ii, 501—502; from *Arch. exp. Path. Pharm.*, 1905, 53, 76—87).—As a result of experiments on frogs and rabbits with a number of quaternary coninium bases such as benzyethylconinium iodide, it is found that there is a reduction in toxic properties with increasing molecular weight. The degree of toxicity depends both on the nature and on the spacial arrangement of the groups attached to the nitrogen atom.

P. H.

Pharmacology of Some Condensation Products of *p*-Aminoacetophenone with Aldehydes. HERM. HILDEBRANDT (*Chem. Centr.*, 1905, ii, 502; from *Arch. exp. Path. Pharm.*, 1905, 53, 87—90).—The anæsthetic properties of aminoacetophenone are not diminished by condensing this substance with aldehydes containing a phenolic hydroxyl, but are destroyed by condensing with other aldehydes, such as benzaldehyde, tolualdehyde, and cinnamaldehyde.

P. H.

Influence of Pilocarpine and Atropine on the Circulation through the Submaxillary Gland. V. E. HENDERSON and OTTO LOEWI (*Chem. Centr.*, 1905, ii, 344—345; from *Arch. exp. Path. Pharm.*, 53, 62—75).—If the *chorda tympani* is stimulated, the vessels of the submaxillary gland enlarge; if atropine is given, this effect is less, not because the dilator nerve-fibres are paralysed, but because secretion falls off. Pilocarpine accelerates the blood-flow and the secretion of saliva; both effects are prevented by atropine. Reasons are given for the deduction that the action of pilocarpine is different to

that obtained by stimulation of the *chorda* nerve endings. The vasodilatation is probably brought about by the action of products due to glandular activity. W. D. H.

Chemical Constitution and Diuretic Action in the Purine Group. PETER BERGELL and PAUL F. RICHTER (*Chem. Centr.*, 1905, ii, 346; from *Zeit. exp. Path. Ther.*, 1, 655—662).—In nephritic rabbits, ethyltheobromine, ethylparaxanthine, and ethyltheophylline act as diuretics. Double salts and other derivatives act similarly, but with different intensities. The intensity of the action depends on the nature of the alkyl residue. W. D. H.

Pharmacology of Sulphones. HERM. HILDEBRANDT (*Chem. Centr.*, 1905, ii, 502—503; from *Arch. exp. Path. Pharm.*, 1905, 53, 90—96).—No alteration in the physiological action of dimethylsulphonedimethylmethane, $\text{CMe}_2(\text{SO}_2\text{Me})_2$, is produced by replacing the methyl groups by ethyl. The author has therefore investigated the effect produced on the physiological action by replacement of methyl by other groups. It is found that the propyl group increases the activity, as also to a lesser extent does the isopropyl group. The introduction of the carbonyl group as in 2:2-diethylsulphone pentane-3-one, $\text{CMe}(\text{SO}_2\text{Et})_2\text{COEt}$, destroys all hypnotic and other noxious properties of the compounds. P. H.

Antagonistic Action of Saponin and Cholesterol. WALTHER HAUSMANN (*Beitr. chem. Physiol. Path.*, 1905, 6, 567—580).—The injurious action of saponin on blood corpuscles is neutralised by cholesterol. This power of cholesterol is increased by the replacement of the hydroxyl group by chlorine, hydrogen, acetyl, or benzoyl radicles. The breaking up of the double linking in cholesterol by chlorine or hydrogen weakens its action. Phytosterol of different origins is antagonistic to saponin. The cholesterol-saponin reaction of Ransom appears to include substances the cholesterol nature of which is uncertain, and to prove that they belong to this group. W. D. H.

Action of Various Nucleic Acids on the Animal Organism. ALFRED SCHITTENHELM and ERNST BENDIX (*Chem. Centr.*, 1905, ii, 840; from *Zeit. exp. Path. Ther.*, 2, 166—178).—Nucleic acid produces a hypoleucocytotic condition followed by a long hypoleucocytosis. The origin of the acid, whether animal or vegetable, does not matter. Sodium α -thymonucleate has no action on blood-pressure, but sodium nucleate from yeast causes it to fall; this is probably due to proteid admixture. After intravenous injection, part passes unchanged into the urine and raises the output of purine bases. The least toxic and the one least harmful to the kidneys of the substances used was Bayer's yeast nucleic acid, and this is poorest in purine bases. W. D. H.

Action of Unaltered Proteid Solutions on the Leucocytes. FRIEDRICH HAMBURGER and A. VON REUSS (*Zeit. Biol.*, 1905, 47, 24—40).—The injection into animals of foreign cells and proteids gives rise to the production of anti-substances, and therefore acts like

a poison. In the present research, certain unaltered proteid solutions, like serum, milk, and white of egg, were injected into rabbits, and the number of leucocytes counted in the blood at intervals after the operation. Rabbits' serum and physiological salt solution gave negative results; horse serum produced a little effect; but the serum of other animals, milk, and egg-white produced a marked lowering of the number of white corpuscles, followed in most cases by a rise later. Whether the disappearance of the leucocytes is due to actual destruction or to their accumulation in the capillary areas of organs due to chemotactic influence was not investigated; but whichever is the correct explanation, the occurrence is evidence of a distinct poisonous action.

W. D. H.

Intravenous Injection of Bone-marrow Extracts. ORVILLE H. BROWN and CHARLES CLAUDE GUTHRIE (*Amer. J. Physiol.*, 1905, 14, 328—338).—The marrow (mostly yellow marrow was used) contains a substance that depresses blood pressure by dilating the blood-vessels; the substance to which this is due is not destroyed by boiling, but its nature is not yet determined. Bone-marrow thus falls into line with most other tissues. In marrow extracts which have not been heated above the body-temperature, there is also evidence of the presence of a pressor substance.

W. D. H.

The Transport of Iodised Fat in Phosphorus Poisoning. H. GIDEON WELLS (*Zeit. physiol. Chem.*, 1905, 45, 412—419).—In rabbits poisoned with phosphorus, the administration of iodised fat leads to an increase in the iodine of liver and kidneys. This is probably due to the fact, not that no transport of fat has occurred, but that, by the action of lipase, the fat first loses its iodine.

W. D. H.

Localisation of Arsenic. GEORGES DENIGES (*Ann. Chim. Phys.*, 1905, [viii], 5, 559—574. Compare Besredka, *Abstr.*, 1900, ii, 156).—The results of the examination of the various organs in human bodies poisoned by arsenic indicate that, whether the poisoning has occurred slowly or rapidly, the arsenic tends to accumulate in the liver, whilst only small quantities are found in the brain and spinal cord. These results are in direct opposition to those of Scolosuboff (this *Journal*, 1876, i, 92). The latter's observations were made on animals poisoned by means of sodium arsenate, and the author has repeated Scolosuboff's experiments on dogs and rabbits, and finds that in these animals, as in man, the poison accumulates in the liver. It is noteworthy that there is generally, between the right and left kidneys, and always between the right and left lobes of the liver, a marked difference in the amount of arsenic present. Particulars are given in the original of the amounts of arsenic found in various organs in a number of cases of poisoning with this material, and there is also a critical *résumé* of previous work on this subject.

T. A. H.

The so-called Antitoxic Action of Bivalent Cations. WILLIAM A. OSBORNE (*Proc. physiol. Soc.*, 1905, x—xii; *J. Physiol.*, 33).—*Fundulus* ova develop in distilled water, but not in pure sodium chloride solutions. If calcium salt is added to the latter, development proceeds normally. From such data, Loeb infers that sodium ions are toxic, whilst calcium (or strontium) ions are antitoxic. A simpler explanation is that in excess of sodium chloride the whole of the calcium in the cell-protoplasm will be eventually replaced by sodium, a change which must profoundly affect the protoplasm; but if calcium and sodium are both present in the outer fluid, the relative concentrations of calcium and sodium in the cell remain unaltered. Some experiments recorded with milk confirm this view. An *iso*-physiological solution must therefore be not only isotonic with the cell contents, but also after it has passed the cell-wall must have its ions in such concentration as to cause no change in the physiological salts and ions within the cell.
W. D. H.

Detection of Hydrocyanic Acid. ANGELO DE DOMINICIS (*Chem. Centr.*, 1905, ii, 265—266; from *Boll. Chim. Farm.*, 44, 337—340).—Working with large animals, hydrocyanic acid can be detected in the blood and organs after it has been administered in various ways. This is contrary to the conclusions of Ganassini (*Boll. Chim. Farm.*, 43, 715).
W. D. H.

The Toxicity of the Normal Intestinal Contents. ERNST MAGNUS-ALSLEBEN (*Beitr. chem. Physiol. Path.*, 1905, 6, 503—523).—The contents and mucous membrane of the upper part of the small intestine of animals fed on flesh, and probably also on bread, fat, and starch-meal, but not on milk or milk-proteid, contain a poisonous substance which, on intravenous injection into rabbits, causes paralysis of the central nervous system and convulsions. Death is due to respiratory stoppage. If the injection is made into the portal vein, the action does not occur, at any rate, with the same doses. The poison is destroyed by boiling in an acid solution. In all regions of the intestine, a substance is also found which lowers blood-pressure; this is not neutralised by passage through the liver, but is destroyed by boiling in an acid solution.
W. D. H.

Thalassin, the Poison of Sea Anemones. CHARLES RICHTER (*Pflüger's Archiv*, 1905, 108, 369—388).—The poison extracted from the tentacles of sea-nettles (anemones) is soluble in 95 per cent. alcohol, and is not destroyed by heat. It is widely distributed in marine animals, and in doses of a thousandth part of a milligram produces poisonous effects of which the most marked is congestion. In large doses, it causes paralysis of the heart. The poison, however, consists of two substances, one of which, named *congestin*, on injection renders an animal more sensitive to the toxic effects, whilst the other, *thalassin*, is of the nature of an antitoxin and produces a certain degree of immunity.
W. D. H.

Antibacterial Sera. W. M. CROFTON (*J. Hygiene*, 1905, 5, 444—450).—There is in inactive immune serum a substance corresponding with immune-substance. A like substance is present in normal serum and in that of patients in an early stage of immunisation. The micro-organism is prepared for phagocytosis by the interaction of two substances, one heat-labile (complement), the other heat-stable (immune-substance). An inactive immune serum is of use in treatment provided the complement is present in the patient's blood-plasma. W. D. H.

Preparation of Cholera Toxin. BRAU and DENIER (*Compt. rend.*, 1905, 141, 397—400).—Vibrios isolated from cholera excreta are capable of furnishing a soluble toxin. The toxin is rendered more active and its production more certain by the introduction of albumins in the cultures of the vibrios. N. H. J. M.

Physical Chemistry of the Toxin-Antitoxin Reaction, with Special Reference to the Neutralisation of Lysin by Antilysin. J. A. CRAW (*Zeit. physikal. Chem.*, 1905, 52, 569—586).—Megatherium lysin (see Todd, Abstr., 1902, ii, 464) passes through a gelatin filter, and can diffuse through gelatin. Megatherium antilysin, on the other hand, does not pass through a gelatin filter, and cannot diffuse through gelatin to any appreciable extent. Filtration and diffusion experiments show that there is free lysin in neutral mixtures of lysin and antilysin, and also in mixtures containing excess of antilysin; further, there is free antilysin in neutral mixtures and also in those containing excess of lysin. The reaction is reversible to some extent when excess of antilysin is present; false equilibria, however, may occur when lysin is present in excess. The neutralisation equation given by Arrhenius and Madsen is not applicable to the case under consideration. The removal of lysin from a solution by antilysin cannot be treated as a purely chemical process. It is closely analogous, however, to certain adsorption phenomena. J. C. P.

Chemistry of Vegetable Physiology and Agriculture.

Decomposition of Vegetable Foods by Bacteria. JOSEF KÖNIG (*Bied. Centr.*, 1905, 34, 698—700; from *Hannov. Land-u. Forstwirtschaftl. Zeit.*, 1904, 37, 627. Compare Abstr., 1903, ii, 386 and 447, and this vol., ii, 472).—In the putrefaction of cotton-seed meal, the non-nitrogenous extract substances and pentosans were chiefly attacked. The nitrogenous matter underwent less complete destruction, the proteids being converted into albumoses, peptones, bases, amides, and ammonia. The fat was least attacked.

N. H. J. M.

Action of Dextrose on the Lactose fermenting Organisms of Fæces. ARTHUR HARDEN (*J. Hygiene*, 1905, 5, 488—493).—*Bacillus coli communis* attacks dextrose in a characteristic way, each molecular proportion of sugar yielding half a molecular proportion of acetic acid, and of alcohol, one molecular proportion of lactic acid, together with small amounts of succinic acid, carbon dioxide, and hydrogen. In view of MacConkey's division of the lactose-fermenting organisms of the intestine into four groups according to their action on sucrose and dulcitol (Abstr., 1905, ii, 601), the present research was undertaken, and it was found that they may be divided into two groups, those which produce alcohol and acetic acid in equal molecular proportion, and those which produce more than 2.5 molecular proportions of alcohol to one of acetic acid. How this fits in with MacConkey's classification is pointed out. *B. lactis aerogenes* acts on dextrose in a totally different way. W. D. H.

Bacteriology of Infectious Gastro-enteritis. HENRI POTTEVIN (*Ann. Inst. Pasteur*, 1905, 19, 426—448).—A species of bacterium, *Bacillus H.*, has been isolated from a ham, the eating of which had produced serious illness. Cultures have been grown in various media, including one with crystal-violet as a component. The effects of such cultures on guinea-pigs, white and grey mice, rabbits, pigeons, pigs, &c., have been studied. The organism can ferment dextrose and mannitol, yielding hydrogen, carbon dioxide, ethyl alcohol, acetic and succinic acids, and large quantities of *l*-lactic acid.

The products obtained by the fermentation of dextrose with *Bacillus enteriditis*, *B. paratyphique* and the bacterium of swine fever are the same as with the bacterium already mentioned. All three organisms are capable of fermenting maltose, dextrose, galactose, mannitol, dulcitol, and, to a certain extent, glycerol. Erythritol, lactose, and sucrose are not fermented.

All the organisms are grouped with the bacilli of swine fever under the generic name *Salmonella* suggested by Lignières. J. J. S.

Isolation of Bacillus Typhosus from Infected Water. H. S. WILLSON (*J. Hygiene*, 1905, 5, 429—443).—The importance of being able to isolate and identify in suspected water the bacillus of typhoid fever is obvious. A new precipitation method is described. The water itself should also be made a nutrient medium by the addition of caffeine (Hoffmann and Ficker), so that the organism multiplies at the expense of others and can thus be detected readily. W. D. H.

Action of Radium Emanations on Pathogenic Bacteria. ERNST DORN, EUGEN BAUMANN, and SIEGFRIED VALENTINER (*Chem. Centr.*, 1905, ii, 841—842; from *Physikal. Zeit.*, 6, 497—500).—Typhoid bacilli are very sensitive to the direct action of radium emanations, but in cultures in gelatin those 2 mm. below the surface are protected. If the emanations are blown through bouillon cultures, their bactericidal action occurs slowly. The same is true for cholera, diphtheria, and other pathogenic organisms. The β -rays are the most harmful.

W. D. H.

Bacteria which are Active in the Maceration of Flax. MARTINUS W. BEYERINCK and A. VAN DELDEN (*Chem. Centr.*, 1905, ii, 843—845; from *Arch. Néerland.*, [ii], 9, 418—441).—The object of maceration is to soften the stems by partial solution and by removing the “pectose.” The latter is a calcium compound related to cellulose, the organic acid of which is a substance of the formula $(C_6H_{10}O_5)_n$ or $(C_{12}H_{22}O_{11})_n$, united with, perhaps, gluconic acid. By treatment with acid, “pectose” yields pectin and metapectin. Pectin gelatinises in presence of lime and pectase, whilst metapectin does not. By further hydrolysis, pectin yields galactose and pentose, other kinds dextrose and arabinose. Both pectose and pectin yield mucic acid when boiled with nitric acid.

The active bacterium in maceration is a granulo-bacterium, *G. pectinovorum*, which dissolves the pectose without injuring the fibre. Its activity is due to a special enzyme, *pectosinase*, which converts pectose successively into pectin and sugar, the bacterium fermenting the sugar with production of hydrogen, carbon dioxide, and a little butyric acid.

The growth of *G. pectinovorum* depends not only on a limited access of air, but also on the previous removal of soluble nitrogenous compounds by immersion of the flax for 24 hours in running water. The temperature should be 28—35°.

The bacterium ferments dilute must, in absence of air, without producing butyric acid. It does not ferment inulin, mannitol, erythritol, glycerol, or gum arabic, but ferments dextrose, lævulose, galactose, lactose, and maltose with peptone, not, however, with ammonia as the source of nitrogen. *G. urocephalum* ferments all kinds of carbohydrates in presence of ammonia. N. H. J. M.

Diastases in Wine Diseases PHILIPPE MALVEZIN (*Chem. Centr.*, 1905, ii, 347; from *Bull. Assoc. Chim. Sucr. Dist.*, 22, 1064—1068).—The micro-organisms which cause diseases of wine, especially *Mycoderma aceti*, *Micrococcus oblongus*, and the mannitol ferment, act probably by means of enzymes specific in causing certain diseases. The two first named produce from dextrose gluconic acid and oxygluconic acid, that is, exert an oxidising action. In lactic fermentation, two molecules of lactic acid arise from one of dextrose, which is regarded as a simple splitting of the molecule, and the name *Pastorase* is suggested for the enzyme. The mannitol fermentation $(C_6H_{12}O_6 + H_2 = C_6H_{14}O_6)$ is due to a *hydrogenase*. W. D. H.

Sterigmatocystis Nigra and Oxalic Acid. P. G. CHARPENTIER (*Compt. rend.*, 1905, 141, 367—369 and 429—431).—*Sterigmatocystis nigra* produces oxalic acid when cultivated in Raulin's liquid, and in the same liquid when the tartaric acid is replaced by sulphuric acid. Oxalic acid is not formed when tartaric acid is the only source of carbon.

Cultivations of *Sterigmatocystis* in Raulin's liquid only secrete oxalic acid when sporulation commences. This is due to the exhaustion of the solution. N. H. J. M.

Lactic Acid Fermentation. E. KAYSER (*Bied. Centr.*, 1905, 34, 701—709; from *Ann. inst. nat. agron.*, [ii], 3, 241).—A ferment is described which assumes various shapes, occurring in spherical forms and in the form of bacilli. It is characterised by the production of ethyl alcohol and mannitol. It is not a real lactic acid ferment, as the amount of lactic acid produced is not more than 70—75 per cent. of the weight of the sugar employed. Both inactive and lævoro-rotatory acids are produced.

Two other ferments are described which yield the dextrorotatory acid, and one which produces the inactive acid. N. H. J. M.

Assimilation of Free Elementary Nitrogen by Micro-organisms. J. VOGEL (*Centr. Bakt. Par.*, 1905, 15, ii, 174—188 and 215—227; this vol., ii, 646).—A *résumé* of the recent investigations on the subject. N. H. J. M.

Loss of Nitrogen in Putrefying Peptone Solutions. Bacteriological Soil Investigation. PAUL EHRENBURG (*Centr. Bakt. Par.*, 1905, 15, ii, 154—164).—The loss of nitrogen in putrefying peptone solutions which have been inoculated with soil and then filtered is due more to absorption than to biological fixation in the soil.

In determining the power of soils to produce putrefaction in peptone solutions, it is necessary to make determinations in the whole contents of the flasks, and to avoid filtration and the use of portions of the solution.

Similar soils, which have been subjected to different treatments, show appreciable differences in their putrefying power. N. H. J. M.

Vegetable Assimilation and Respiration. IV. Carbon Dioxide Assimilation and Leaf Temperature. F. FROST BLACKMAN and GABRIELLE L. C. MATTHAEI (*Proc. Roy. Soc.*, 1905, 76 B, 402—460).—Three factors control the amount of assimilation of carbon dioxide by a leaf: (1) intensity of illumination, (2) temperature of the leaf, and (3) pressure of the gas in the surrounding air. The present work is an attempt to interpret the quantitative variations in terms of the three factors. Differences are noted between leaves of different plants in their coefficients of acceleration of assimilation activity with increase of temperature. There is no optimum intensity of light for assimilation, but equal intensities incident upon equal areas of different leaves produce equal amounts of assimilation. W. D. H.

Pure Culture of Green Plants, in a Confined Atmosphere, in Presence of Organic Matters. MOLLIARD (*Compt. rend.*, 1905, 141, 389—391. Compare *ibid.*, 1904, 139).—When a plant is grown in a solution containing 10—15 per cent. of dextrose, the decomposition of carbon dioxide is four times as great (for the same leaf-surface) as with a purely mineral solution.

In cultures containing asparagine in addition to dextrose, there is a much greater absorption than when dextrose alone is supplied.

In absence of light, the absorption of sugar is very small.

N. H. J. M.

Different Origin of the Carbon Dioxide given off by Plants during Respiration. WLADIMIR PALLADIN (*Chem. Centr.*, 1905, ii, 639; from *Ber. deut. bot. Ges.*, 23, 240—247).—The carbon dioxide given off by plants is attributed to different sources. [(1) Nucleo-carbon dioxide produced by enzymes united with the protoplasm; (2) from protoplasm under the influence of various irritants, and (3) oxydase-carbon dioxide produced by catalase and oxydase, &c.]

It was found that the elimination of carbon dioxide increases with the amount of protoplasm. Sap from bulbs of *Gladiolus Lemoinei* which gives off only traces of carbon dioxide, produces considerable amounts of the gas when hydrogen peroxide is added. Pyrogallie acid produces a similar effect. N. H. J. M.

Effect of Carbon Dioxide on Geotropic Curvature of the Roots of *Pisum Sativum*. ERIC DRABBLE and HILDA LAKE (*Proc. Roy. Soc.*, 1905, B, 76, 351—358).—When roots are placed horizontally in boiled water or in hydrogen or other indifferent gas, they fail to respond to geotropic stimulus. When removed from the boiled water and placed vertically in air, the root curves in the direction of the previous stimulus.

The object of the experiment now described was to ascertain the effect of carbon dioxide on geotropic curvature. The roots, in a horizontal position, were subjected to the action of air containing various amounts of carbon dioxide for different lengths of time and then placed in a klinostat, which revolved once in 19 minutes, so that the axis of the root was parallel to the axis of rotation. The first appearance and extent of the earlier curvatures were then observed. In air and with amounts of carbon dioxide up to 3 per cent., all the roots finally showed large curvatures, whilst with 7.5 and 10 per cent. of carbon dioxide the actual power of response was greatly diminished as well as delayed. The measurements of the curvatures observed after 30 minutes and at intervals up to three hours are given in tables.

It is considered that the effects produced may not improbably be attributed to the positive or negative ion (H^+ or HCO_3^-) of dissociated carbonic acid. N. H. J. M.

Lime Requirements of Plants. OSCAR LOEW (*Bied. Centr.*, 1905, 34, 651—654; from *Landw. Jahrb.*, 1905, 34, 131—137).—An excess of calcium in plants is in most cases rendered harmless by conversion into oxalate, whilst an excess of magnesium will retard growth.

Soils which contain approximately the same amounts of calcium and magnesium are most suitable for cereals. In the case of leaf crops, an excess of calcium over magnesium (2—3 : 1) is desirable.

N. H. J. M.

Lime Requirements of Various Vegetable Organs. OSCAR LOEW (*Chem. Centr.*, 1905, ii, 412—413; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 8, 603—608).—According to Wolff's tables, barley and peas (without the roots) contain far more calcium than magnesium, especially in the leaves. The roots contain much less calcium than the leaves, but usually contain a good deal more calcium than magnesium. The seeds alone show an excess of magnesium.

It has been found that the roots grow much more in presence of an excess of magnesium than with an excess of calcium, whilst the stems and leaves diminish.

N. H. J. M.

An Electrical Response to Excitation in *Desmodium Gyrams*. FLORENCE BUCHANAN (*Proc. Physiol. Soc.*, 1905, viii—x; *J. Physiol.*, 33).—A study of the electrical changes which occur on stimulating the stipellæ of the leaflets. The rate of propagation of the change has not yet been studied. Cells with protoplasmic connections capable of conducting impulses in the direction of the fibro-vascular bundles were found by Haberlandt in *Mimosa*. Similar appearances are found in *Desmodium*. The characteristic leaf-movements in the latter can be induced in an inactive plant by supplying the roots with water containing 0.05 per cent. of ammonia. Stahl explains the movement by regarding it as an adaptation for increasing transpiration and supplying nutritive salts to the leaves. The supply of nutrient and other solutions, however, appears more likely to be the cause rather than the effect of the movement. W. D. H.

Reactions of Living Cells to Dilute Solutions of Heavy Metallic Salts. THOMAS BOKORNY (*Chem. Centr.*, 1905, ii, 833; from *Pharm. Centr.-H.*, 46, 605—609. Compare Abstr., 1905, ii, 476).—Work on the same lines as previously published, special attention being paid to the action of salts of copper, mercury, and silver.

After exposure of *Spirogyra* and other cells to the action of dilute silver nitrate, the position of the silver compounds formed can be subsequently localised microscopically by treatment with hydrochloric acid and hydrogen sulphide, or sunlight.

W. D. H.

Existence in Red-currants of a Compound yielding Hydrogen Cyanide. L. GUIGNARD (*Compt. rend.*, 1905, 141, 448—452. Compare this vol., ii, 604).—Leaves of red-currants yield hydrogen cyanide at all periods of vegetation, but the amount is always small, being 0.0035 per cent. in the middle of June, 0.0026 per cent. some weeks later, and 0.0015 per cent. at the beginning of August; the young twigs yield very little and the roots none at all.

Leaves of *Ribes aureum* also yield hydrogen cyanide, but in smaller quantity than red-currants. Negative results were obtained with leaves of *Ribes nigrum*, *R. Uva-crispa*, *R. sanguineum*, *R. multiflorum*, *R. subvestitum*, *R. prostratum* and *R. Gordonianum*.

N. H. J. M.

Coto Bark. OSWALD HESSE (*J. pr. Chem.*, 1905, [ii], 72, 243—248. Compare Jobst and Hesse, Abstr., 1880, 325; Hesse, Abstr., 1895, i, 110; Ciamician and Silber, *ibid.*, i, 554).—The author describes a new coto bark which comes from the same district of Bolivia as the true coto bark, but does not contain cotoin. It has a pleasant, aromatic odour, and when treated with ether yields benzoic acid and a neutral substance, *cotellin*, $C_{18}H_{16}O_4(OMe)_2$. This crystallises in glistening, tetragonal, double pyramids, or from dilute alcohol in colourless leaflets, has no taste, melts at 169°, and decomposes at a few degrees higher. It is moderately soluble in hot alcohol, ether, acetone, or glacial acetic acid, and dissolves easily in chloroform or benzene. It

does not dissolve in dilute alkali hydroxides or acids, but with concentrated sulphuric acid forms a yellow solution which becomes brownish-black ; it evolves red vapours and forms oxalic acid and a yellow, resinous mass when warmed with concentrated nitric acid, and yields a bluish-green substance when heated with concentrated potassium hydroxide.

With bromine in chloroform solution, cotellin forms a *tetrabromo-derivative*, $C_{20}H_{16}O_6Br_4$, which crystallises in small, white needles, and melts and decomposes at 220° ; when treated with concentrated sulphuric acid it becomes yellow, and when warmed, black, and it forms a brownish-black mass when evaporated with aqueous potassium hydroxide.

When warmed with acetic anhydride at 85° , the crystalline cotellin is converted into an amorphous modification which melts at about 80° .

G. Y.

Proteids of the Castor Bean ; Isolation of Ricin. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and ISAAC F. HARRIS (*Amer. J. Physiol.*, 1905, 14, 259—286).—The proteids are like those of other oil-beans, and consist of a crystallisable globulin, a smaller amount of coagulable albumin, and proteoses. Ricin is believed to be identical with the albumin ; a new method for isolating it to study its agglutinating and toxic characters (which are very powerful) is given.

W. D. H.

The Hydrolytic Enzyme, Lipase. FREDERICK L. DUNLAP and WILLIAM SEYMOUR (*J. Amer. Chem. Soc.*, 1905, 27, 935—946).—Four seeds were examined in a resting state and two of them in a germinated condition. Flax, pea-nut, croton, and almond seeds are not hydrolytic, or only very slightly so in a resting state, and the zymogen is not rendered active by the means utilised for castor-oil bean, celandine, and toad-flax.

Lipase is produced during the germination of flax and pea-nut, and active solutions were prepared. It is probable that the lipase differs from that of the bean ; the solutions, both from flax and from pea-nut, are precipitated by alcohol, but whilst the precipitate in pea-nut lipase shows marked lipolytic power, that in flax lipase solutions does not.

N. H. J. M.

Cause of the Presence of Abnormal Amounts of Starch in Bruised Apples. G. WARCOLLIER (*Compt. rend.*, 1905, 141, 405—408).—When apples are bruised, the tannin coagulates the amylase, and thus prevents the transformation of starch into fermentable sugars.

N. H. J. M.

Dampness of Grain. J. E. HOFFMANN (*Bied. Centr.*, 1905, 34, 688—692 ; from *Wochens. Brau.*, 1905, No. 18).—Wetness of grain is due to conditions of weather, the moisture deposited on the cold grain from warm and damp air being rapidly absorbed, and to respiration. The water thus absorbed is given off later on when the weather becomes warmer.

Absorption of water results in the production of maltose, whilst elimination of water gives rise to production of starch (compare Grüss, *Woch. Brau.*, 1899, 519).

N. H. J. M.

Development of Rye and Wheat. BERNHARD SCHULZE (*Bied. Centr.*, 1905, **34**, 602—610; from *Landw. Jahrb.*, 1904, 405).—By the end of the winter, rye had assimilated nearly half of the final amount of nitrogen, whilst in the case of wheat, assimilation of nitrogen took place chiefly from the beginning of April to the commencement of grain production. It is therefore desirable to provide rye with soluble nitrogen during winter. Both crops would have plenty by the beginning of spring. Phosphoric acid is chiefly taken up during spring growth by rye and until after flowering by wheat. Both rye and wheat take up certain amounts of potassium in the winter, but chiefly at the time of the greatest production of carbohydrates. Calcium and magnesium are less in demand by the young plants and are probably, like silica, of more importance later on, in connection with the solidification of the tissues.

N. H. J. M.

Variability of Wheat Varieties in Resistance to Toxic Salts. L. L. HARTER (*Bureau of Plant Industry, Bul.* 79, *U.S. Dept. Agr.*, 1905).—The salts with which experiments were made are injurious to wheat seedlings in the following order: magnesium sulphate, magnesium chloride, sodium carbonate, sodium hydrogen carbonate, sodium sulphate, sodium chloride. In the case of other plants, the order may be different. Wheat is one and a half to six times as resistant as white lupins; the least difference is with sodium carbonate and the greatest with magnesium sulphate and sodium hydrogen carbonate.

Different varieties of wheat, representing extremes, vary in the ratio 1 : 3 in their power of resistance; but varieties which as a whole are the most resistant are not always the most resistant to every salt. Similarly, the generally least resistant is not necessarily the least resistant to each salt.

All the salts employed, except sodium carbonate and chloride, act as stimulants in dilute solutions. Pure water does not hinder development, but traces of zinc will kill the root-tips in 24 hours.

N. H. J. M.

Durum Wheat. F. A. NORTON (*J. Amer. Chem. Soc.*, 1905, **27**, 922—934).—The amount of proteids in Durum wheat is much higher than in bread wheats, and tends to increase under American conditions of soil and climate. The wheat is especially rich in sucrose and dextrose; the gluten is high, but of rather poor quality, being deficient in gliadin. This deficiency seems, however, to be compensated for in the best wheats by greater amounts of gluten. The best Durum wheats are very suitable for bread and macaroni.

N. H. J. M.

[Pot-culture Experiments on the Influence of the Iodides and Oxides of Manganese, Potassium, Sodium, and Lithium on Wheat and Barley.] JOHN A. VOELCKER (*Jour. Roy. Agric. Soc. Engl.*, 1904, **65**, 306—314).—The salts were mixed with the last four pounds of the soil used in filling the pots so as to avoid possible removal beyond the reach of the roots in their early stages.

Manganese, potassium, sodium, and lithium are injurious to wheat when applied at the rate of 1 cwt. per acre, and to barley when 2 cwt. per acre are applied. In the case of wheat, the manganese salt is the most injurious. The corresponding oxides, especially lithium oxide, are beneficial to wheat when applied at the rate of 2 cwt. per acre. With the exception of lithium oxide, which is possibly beneficial, the oxides had no effect on barley.

The results of water-culture experiments on barley with lithium and manganese iodides and oxides (0.1 to 0.2 gram per litre) show that the iodides are poisonous, and that the oxides are without much effect. Manganese salts produce long, wiry roots, whilst lithium salts give rise to thick, stunted roots.

N. H. J. M.

Influence of the Composition of Barley on the Development, Quality, and Productivity, and on the Transmission of these Properties. JOHANN VAÑHA, OTTO KYAS, and JOSEF BUKOVANSKY (*Chem. Centr.*, 1905, ii, 695—696; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 8, 667—684).—The yield of barley increases with the amounts of non-nitrogenous extract substances and soluble proteids in the seeds. A high percentage of extract in the seed is favourable to the lengthening of the stems, whilst the number of ears increases with the soluble proteids of the seed.

Seeds with high amounts of extract and of proteids do not yield crops with high extract and high proteid.

N. H. J. M.

Pot Experiments to Determine the Limits of Endurance of Different Farm-crops for Certain Injurious Substances. FREDERICK B. GUTHRIE and R. HELMS (*Agric. Gaz. N. S. Wales*, 1905, 16, 853—860. Compare *ibid.*, 1903, 14, 114, and 1904, 15, 29).—Barley and rice were grown in a mixture of garden loam and sand, to which superphosphate and varying amounts of sodium chloride, sodium carbonate, sodium chlorate, and arsenious oxide respectively were added. The results are summarised in the following table, in which the numbers indicate percentages of the different substances employed :

		NaCl.	Na ₂ CO ₃ .	NaClO ₃ .	As ₂ O ₃ .
Germination affected	{ barley	0.1	0.25	0.005	—
	{ rice	0.1	0.25	0.004	0.2
Germination prevented	{ barley	0.25	0.60	0.007	0.6
	{ rice	0.40	0.50	0.006	0.4
Growth affected	{ barley	0.10	0.15	0.003	0.05
	{ rice	0.15	0.25	0.002	0.15
Growth prevented	{ barley	0.20	0.40	0.006	0.10
	{ rice	0.20	0.40	0.004	0.30

N. H. J. M.

Plant Analysis as an Aid in Estimating the Manurial Requirements, with Special Reference to Hops. PH. SCHNEIDER (*Chem. Centr.*, 1905, ii, 970—971; from *Woch. Brau.*, 22, 456—458).—The amount of phosphoric acid in the more advanced leaves of hops

shows a definite minimum, about 0.5 per cent. in the lower leaves, when phosphoric acid is deficient in the soil. At the time of the first crop, the lower leaves showed the optimal stage of development, whilst at the time of the second crop the upper leaves reached the stage at which a deficiency of phosphoric acid is best observed.

The amount of nitrogen in hops follows that of phosphoric acid, and the deficiency or otherwise of nitrogen in the soil is best detected by the composition of the leaves. No definite results can, however, be obtained in the case of potassium, magnesium, and calcium.

N. H. J. M.

Ripening of Peaches. WILLARD D. BIGELOW and HERBERT C. GORE (*J. Amer. Chem. Soc.*, 1905, 27, 915—922).—The samples were collected (1) in June, after all the imperfect fruit had fallen off; (2) when the stone had hardened; and (3) when ripe for the market. The average weights (six varieties) at the three periods were 9.51, 16.75, and 73.59 grams, and the weights of flesh were 6.12, 11.89, and 68.11 grams respectively.

The percentage composition of the flesh was as follows:

	Solids.	Reducing sugar.	Sucrose.	Acid (as H_2SO_4).	Proteids.	Amides.	Ash.
1.	14.77	2.71	0.18	0.28	0.77	0.21	0.75
2.	16.97	2.26	1.57	0.34	0.63	0.18	0.68
3.	14.04	1.98	5.70	0.56	0.27	0.08	0.40

N. H. J. M.

Etherisation as an Aid in Rhubarb Forcing. WILLIAM STUART (*17th Ann. Rep. Vermont Agric. Exper. Stat.*, 1903—1904, 442—445).—The plants were dug up late in the autumn and subjected to frost in the usual manner, in a cold frame. The first lot was placed in a cool cellar to thaw and subjected to ether (10 c.c. per cubic foot of air) for 48 hours (Dec. 20). The plants were then placed in a darkened greenhouse having a temperature of 45—65°. Three other lots were etherised on Jan. 9, Jan. 30, and Feb. 24 respectively.

The results of experiments 1, 2, and 4 showed a gain of 622 per cent. in the first cutting, and of 86, 23, and 47 per cent. in the second, third, and fourth cuttings respectively, due to etherisation. It is probable that still greater increase would be obtained by treating with ether at a still earlier date.

In the third experiment, a larger amount of ether (17 c.c. per cubic foot of air) was employed: the results were much less satisfactory.

N. H. J. M.

Cultivation of *Solanum Commersoni* at Verrières (Vienne, France). LABERGERIE (*Bied. Centr.*, 1905, 34, 616—622; from *Jour. d'Agr. prat.*, 68, 631, 665, 803, and 831).—The original plant brought by Heckel in 1901 from Uruguay has yellowish-white, egg-shaped tubers, having a very bitter taste. By cultivation, an edible variety has been obtained, equal at least to potatoes. It is better

able to resist disease than potatoes, yields larger crops, and is more nutritious. The average yield of starch is 15,000 kilos. per hectare.

The composition of tubers grown on good soil was as follows : water, 72.59 ; starch, 19.91 ; sugar, 0.114 ; fat, 0.022 ; and crude fibre, 0.639 per cent. N. H. J. M.

Results of Experiments on the Action of Phosphoric Acid on Sugar Beet. HERMANN RÖMER (*Chem. Centr.*, 1905, ii, 851 ; from *Zeit. Ver. Rüben Zucker-Ind.*, 1905, 764—774).—The experiments were made in a mixture of sand and peat. Without phosphoric acid, the average weight of the roots was 0.36 gram, and they contained 6.5 per cent. of sugar. The leaves were dark green. With very small amounts of phosphoric acid, the roots weighed 24 grams and contained 14.3 per cent. of sugar. The amount of phosphoric acid required is probably between 0.568 and 1.065 grams per root ; or 12.5 to 19 kilos. per morgen to obtain a yield of 200 cwt.

N. H. J. M.

Feeding and Metabolism of Agricultural Animals. FRANZ TANGL (*Bied. Centr.*, 1905, 34, 671—692 ; from *Landw. Jahrb.*, 1905, 1—92).—*Sorghum* [with STEPHAN WEISER and ARTHUR ZAITSCHEK].—The available chemical energy of sorghum is, for bullocks, 59.7 ; sheep, 56.5 ; horses, 61.8 ; pigs, 68.7 ; ducks, 46.7 ; and geese, 57.1 per cent. In the case of bullocks, the utilisation is less when more than 6 kilos. per 1000 kilos. of live weight is given. It gave better results (although less economical) than maize for fattening cows. For horses, a mixture of oats (2) and sorghum (1 part) is recommended. It is a suitable food for pigs, geese, and turkeys, but not for poultry and ducks.

Composition and Nutritive Value of Oats [with MICHAEL KORBULY and STEPHAN WEISER].—The amounts of constituents of oats digested by (1) horses and (2) sheep are as follows :

	Organic matter.	Crude protein.	Crude fat.	Crude fibre.	Non-nitrog. extract.	Pentosans.	Energy per kilog.
1.	50.58	7.76	3.22	0.78	38.82	1.68	2421 Cal.
2.	56.20	7.25	3.73	4.41	40.81	4.00	2660 „

Of the total energy of oats, horses utilise 54.8 and sheep 53.85 per cent. The weight per hectolitre of oats has no relation to the composition. N. H. J. M.

Effect of Asparagine on the Production of Milk and its Constituents. THEODOR PFEIFFER, A. EINECKE, and W. SCHNEIDER (*Mitt. landw. Inst. k. Univ. Breslau*, 1905, 3, 179—225).—The partial substitution of proteids, in a ration moderately rich in proteids, by a caloric equivalent mixture of asparagine and sucrose did not diminish the yield of milk ; in some cases there was, perhaps, an increase. The percentage and absolute amount of milk fat was diminished, and there was a reduction in the percentage of proteids and dry matter, but no essential change in the absolute amount of proteids. The substitution acted unfavourably on the increase in live-weight.

The conclusion is drawn that amides should not be considered as nutritive substances, although in very nutritive rations they act, in some unexplained manner, as stimulants, and are favourable to milk production at the expense of other constituents of the food and body.

N. H. J. M.

Sterilisation of Milk with Hydrogen Peroxide, with Special Reference to Budde's Process. MISTISLAW LUKIN (*Centr. Bakt. Par.*, 1905, 15, ii, 165—174. Compare this vol., ii, 647).—Hydrogen peroxide is more active in neutral or slightly alkaline solutions than in acid solutions; ordinary solutions should therefore be neutralised when used. The temperature 52° (Budde) is the most favourable, and in most cases 12 c.c. of 3 per cent. hydrogen peroxide is sufficient for 1 litre of milk.

The objections to Budde's process are the small amounts of unchanged hydrogen peroxide in the sterilised milk and the presence of injurious substances (arsenic and barium chloride) in ordinary preparations of hydrogen peroxide. The consumption of the sterilised milk is not known to have had injurious effects; it is, however, desirable that the changes which are known to occur in the proteids should be further investigated.

N. H. J. M.

Comparative Experiments on Chemical Preservatives in Milk. HENRY C. SHERMAN, ALBERT W. HAHN, and ARTHUR J. METTLER (*J. Amer. Chem. Soc.*, 1905, 27, 1060—1068).—Milk kept at 20—25° without preservative rapidly lost lactose and gained in acidity during the first three to six days; the destruction of lactose then proceeded more slowly, but the formation of acid had not ceased entirely after four weeks.

0.1 per cent. of hydrogen peroxide, sodium fluoride, sodium salicylate, or a mixture of equal parts of boric acid and borax distinctly diminished the development of acidity in milk. Except in the case of hydrogen peroxide, which rapidly disappears, the amount of added preservative can be determined with a fair degree of accuracy by the usual methods. In the case of fluoride or salicylate preservative, the occasional opening of the bottles led to irregular results. For details, the tables contained in the original paper should be consulted.

L. DE K.

Classification and Nomenclature of Arable Soils according to their Mineral Constitution. H. LAGATU (*Compt. rend.*, 1905, 141, 363—366. Compare this vol., ii, 557; and Delage and Legatu, *Constitution de la terre arable*, Montpellier, 1904).—A graphic method for the representation of the amounts of chalk, clay, and sand is described.

N. H. J. M.

Diffusion in Acid and Neutral Media, especially in Humus Soils. HERMANN MINSEN (*Landw. Versuchs-Stat.*, 1905, 62, 445—476).—It is shown that neither free humic acid nor other acids (organic and mineral) in dilute solutions have a retarding effect on the rate of diffusion of water or of solutions of salts. The "physiological

dryness" of peat soils cannot, therefore, be due to free humic acid. The far-reaching conclusions which have been drawn respecting the action of free humic acid on the growth of plants do not, therefore, hold good.

N. H. J. M.

Insoluble Alkaline Compounds formed by Humic Substances and their Rôle in Vegetable Physiology and Agriculture. MARCELLIN BERTHELOT (*Compt. rend.*, 1905, 141, 433—445).—Potassium and calcium displace each other both in soluble and insoluble compounds, according to their proportions and the relative strengths of the mineral, organic, and humic acids.

The potassium of soluble compounds may be rendered insoluble by humic substances and thus stored for a time. It is again rendered available by double decomposition and by the spontaneous oxidation of the organic matter, the potassium then being converted into carbonate. Analogous changes occur at the expense of the calcium present in the soil as carbonate, silicate, sulphate, and phosphate, &c., or as humates.

Potassium and calcium are not directly appropriated by humic acid when in combination with strong acids. The displacement may, however, occur by the intervention of ammonia, by means of which the stronger acids are eliminated; coincidentally, amino-humic acids are formed which are capable of rendering potassium insoluble.

N. H. J. M.

Absorptive Power of Soils for Bone and Mineral Superphosphates. CARLO MONTANARI (*Chem. Zeit.*, 1905, 29, 988—989).—A preliminary communication. The popular idea as to the greater activity of bone superphosphate is not supported by facts. It now, however, appears that the phosphoric acid from mineral superphosphates is not quite so rapidly absorbed by the soils, although on the other hand the portion absorbed is more readily taken up by the roots.

L. DE K.

Asparagine Substances [Amino-acids in Molasses]. PROBERTI (*Chem. Centr.*, 1905, ii, 773; from *Bull. Assoc. Chim. Sucr. Dist.*, 22, 1163—1186).—Molasses obtained in 1903 contained *N* 1.388, and *N* as amino-acids 0.969 per cent. In 1904, the amounts were 1.946 and 1.369. The high amounts of nitrogen in 1904 were coincident with a low amount of alkali. This is attributed to the roots having suffered from drought followed by heavy rainfall, conditions unfavourable to assimilation being favourable to the production of amino-acids.

N. H. J. M.

Action of Sodium Chloride on Crops. FERDINAND WOHLTMANN (*Bied. Centr.*, 1905, 34, 656—658; from *Landw. Zeit. Rheinprov.*, 1904, Nos. 46 and 47).—Sodium chloride did not benefit cereal crops and injured potatoes both as regards yield and quality. It was very beneficial in the case of sugar beet and mangolds.

N. H. J. M.

Lime Manuring. OSKAR LOEW (*Chem. Centr.*, 1905, ii, 412; from *Zeit. landw. Versuchs-Wes. Oesterr.*, 8, 583—602).—Application of lime is desirable when the soil contains twice as much or more magnesium as calcium. Magnesia should be applied when there is a considerable excess of calcium present, even if the actual amount of magnesium in the soil is sufficient for a crop. When there is a deficiency both of calcium and magnesium, dolomite may be used with advantage.

N. H. J. M.

Analytical Chemistry.

Colorimetric Methods; a Simple Colorimeter for General Use. OSWALD SCHREINER (*J. Amer. Chem. Soc.*, 1905, 27, 1192—1203).—An improved colorimetric apparatus, for details of which the original article and illustration must be consulted. L. DE K.

New Gas-absorption Apparatus. ROMUALD NOWICKI (*Chem. Centr.*, 1905, ii, 919; from *Österr. Zeit. Berg. Hütt.*, 53, 337—338. Compare Abstr., 1904, ii, 555).—Improved Orsat apparatus in which the gaseous mixture passes through a capillary-tube into the absorbing liquid. For further particulars the original article and illustrations should be consulted. L. DE K.

Action of Concentrated Hydrochloric Acid on Potassium Chlorate in the Presence of Potassium Iodide or Bromide; Estimation of Chlorates. HUGO DITZ (*Zeit. angew. Chem.*, 1905, 18, 1516—1520).—A criticism of Kolb and Davidson's paper (this vol., ii, 59). L. DE K.

Inner Crucible Method for Estimating Sulphur and Halogens in Organic Substances. SAMUEL S. SADTLER (*J. Amer. Chem. Soc.*, 1905, 27, 1188—1192).—The outer crucible is made with straight sides like an inverted truncated cone with a tightly fitting lid. In the bottom is a cylindrically-shaped indentation so as to extend the highly heated zone into the inner crucible. The latter is made with sides very nearly parallel to the outer crucible when inverted within it. Small rings of platinum are soldered to the wide closed end so as to keep it centred with respect to the outer one. The wall at the open end is made as thin as possible so as to minimise the tendency to conduct heat. The edge fits about midway between the walls of the central indentation and the outer crucible.

A quantity of substance, solid or liquid, representing about 0.01 gram of sulphur or 0.05 gram of phosphorus or halogen is weighed in the inner crucible. The crucible is then filled nearly to the top with a mixture of equal parts of dry sodium carbonate and magnesium oxide. Plain magnesia is then put in level with the top so as to keep the soda away from the platinum. Ignited asbestos is put round the

raised portion of the bottom of the outer crucible to keep the two crucibles from being in actual contact. It is then lowered over the inner crucible and both crucibles inverted. A layer of the magnesia-soda mixture about one-fourth inch deep is put between the crucibles. The outer crucible is put through a hole in a piece of thin asbestos board so that the sides shall not be exposed to the direct action of the flame.

A very small pointed flame of a Bunsen burner is now applied to the indentation on the bottom, and after a few minutes the heat is increased, and finally the crucible is placed in a piece of asbestos having a larger hole, so that half of the crucible may get red hot. After ten minutes, the flame is withdrawn.

The sulphates, phosphates, chlorides, &c., formed are estimated by the usual processes. L. DE K.

Gravimetric Estimation of Sulphur in Iron and Steel.

CHARLES R. MCCABE (*J. Amer. Chem. Soc.*, 1905, 27, 1203—1204).—To prevent the escape of unoxidised sulphur during the period of the violent action of the nitric acid, 5 grams of drillings are placed in a litre flask fitted with a doubly perforated cork which has been slightly charred on its inner end. In one perforation is fitted a funnel tube with a stopcock; in the other is fitted a piece of quarter-inch glass tubing which extends about 18 inches above the flask and is drawn to a point at the end projecting out of the flask. The stopcock being closed, 50 c.c. of strong nitric acid are introduced into the funnel tube. The acid is now run into the flask at the rate of about two drops per second. When all the acid has passed into the flask, the stopcock is closed and the flask heated gently until complete solution has taken place.

The contents are evaporated in a porcelain dish with addition of hydrochloric acid, and the sulphuric acid is then estimated by means of barium chloride as usual. L. DE K.

Estimation of Sulphur in Pyrites. MAX DENNSTEDT and F. HASSLER (*Zeit. angew. Chem.*, 1905, 18, 1562—1564).—The sample is heated in a current of oxygen in a Dennstedt combustion tube (*Abstr.*, 1903, ii, 103), and the products of combustion are absorbed in four small boats filled with dry sodium carbonate and heated at about 300°. The sulphate formed is then estimated as usual. The iron oxide left in the boat is apt to retain a not inconsiderable amount of sulphur trioxide, which must then be estimated by Lunge's method (precipitation with barium chloride after removing the iron with ammonia).

Instead of sodium carbonate, lead dioxide may be used as an absorbent. After treating it with a 5 per cent. solution of sodium hydroxide, the sulphuric acid dissolved in the alkaline liquid is estimated as usual. L. DE K.

Estimation of Sulphur in Liquid Fuel and in Petroleum.

ALBERTO GOETZL (*Zeit. angew. Chem.*, 1905, 18, 1528—1531).—Two to three grams of the liquid fuel are placed in a spacious platinum crucible, and 4 c.c. of fuming nitric acid are added. As the reaction is

rather violent, the crucible should be covered with a watch-glass. When no further action is noticed, the crucible is heated on a water-bath, and when finally all action has ceased the watch-glass is removed and the excess of acid is evaporated. The mass is then mixed with 6 to 8 grams of a mixture of ten parts of dry sodium carbonate and two parts of nitre, and after sprinkling more of this mixture on the surface, the whole is gradually heated to fusion. The mass now contains the sulphur as sulphuric acid, which is estimated as usual.

When testing petroleum, about 10 grams should be taken for analysis.

L. DE K.

Estimation of Sulphur in Coal. OTTO BRUNCK (*Zeit. angew. Chem.*, 1905, 18, 1560—1562).—One gram of the finely powdered sample is mixed intimately with 2 grams of a mixture of two parts of cobaltic oxide and one part of dry sodium carbonate. The cobalt oxide must be prepared by gently igniting cobalt nitrate. The mixture is placed in a boat and then heated in a current of oxygen until the carbon has burnt off. If desired, the products of combustion may be passed through a hydrochloric acid bromine solution and a solution of sodium hypobromite to retain traces of volatilised sulphur compounds.

The residue is then extracted with water and, after adding a few c.c. of hydrogen peroxide to fully oxidise the sulphur, the filtrate is acidified with hydrochloric acid and treated with barium chloride as usual.

L. DE K.

Estimation of Nitric Acid in the Presence of Organic Matter. BALTHASAR PFYL (*Zeit. Nahr.-Genussm.*, 1905, 10, 101—104).—The solution containing the nitric acid (nitrates) is boiled in a small flask until all air has been expelled and the volume of the solution reduced to about 5 c.c. During this time, the delivery tube of the flask is placed below the surface of water. By means of a clamp, the water is prevented from entering the flask when the flame is removed. After the contents of the flask have cooled somewhat, 20 c.c. of a solution containing 30 grams of ferrous chloride in 50 c.c. of dilute hydrochloric acid (2:3) are allowed to enter and the closed flask is heated in a water-bath for 45 minutes. Ten c.c. of boiled dilute sulphuric acid (1:4) are then introduced, and the end of the delivery-tube is inserted under a bell-jar filled and surrounded with a 15 per cent. sodium hydroxide solution, which has been previously boiled. On heating the contents of the flask, the nitric oxide is evolved and collected under the bell-jar. From the top of the latter, an outside tube leads downwards with its end dipping under the neck of a flask filled with boiled sulphuric acid (1:4) and inverted in a vessel also containing sulphuric acid and a measured volume of *N*/10 potassium permanganate solution. The gas is driven out of the bell-jar into the inverted flask (where it is absorbed by the permanganate) by increasing the volume of the sodium hydroxide solution surrounding the bell-jar. After completing the absorption by cautiously shaking the flask, the excess of permanganate is titrated back with *N*/10 ferrous chloride solution. *N*/10 Permanganate corresponds with 1/30 KNO_3 or 1/60 N_2O_5 .

W. P. S.

Detection of Nitrates by Diphenylamine. CARL G. HINRICHS (*Bull. Soc. chim.*, 1905, 33, 1002—1005).—For use as a reagent, diphenylamine is dissolved in glacial acetic acid. This solution produces a blue coloration when added to such oxidising substances as nitrites, peroxides of hydrogen, sodium, barium, manganese or lead, chromates, dichromates, molybdates, vanadates, permanganates, chlorates, perchlorates, ferricyanides, or iodates in concentrated sulphuric, phosphoric, or hydrochloric acid at the ordinary temperature, whereas diphenylamine gives a blue coloration with nitrates in concentrated sulphuric or phosphoric acid at the ordinary temperature, but in concentrated hydrochloric acid only on warming to 50° , or with traces of nitrates on boiling.

Similarly, brucine or ferrous sulphate reacts with nitrates in concentrated hydrochloric acid only on heating. Brucine gives no reaction with nitrites, but with vanadates a yellow colour is formed, which becomes red on addition of concentrated hydrochloric acid. Ferricyanides give similar reactions. G. Y.

Estimation of Phosphorus in Phosphorised Oil. HENRIK ENELL (*Chem. Centr.*, 1905, ii, 570—571; from *Pharm. Zeit.*, 50, 601—603).—One gram of the sample is dissolved in a mixture of 10 c.c. of alcohol and 20 c.c. of ether, a drop of phenolphthalein solution is added, and then 12 c.c. of $N/10$ iodine solution. After shaking for a few minutes, the excess of iodine is carefully removed by means of $N/10$ thiosulphate and the acid formed is titrated with $N/10$ sodium hydroxide. Any acid already present in the sample is estimated by dissolving one gram of the oil in 10 c.c. of alcohol and 20 c.c. of ether. Twenty c.c. of water and a drop of phenolphthalein are added, and the whole is well shaken and titrated with sodium hydroxide.

The difference between the two titrations represents the phosphorus. 16.12 c.c. of $N/10$ alkali equal 0.01 gram of phosphorus. L. DE K.

Estimation of Phosphorus in Phosphorised Oil. ERWIN RUPP (*Chem. Centr.*, 1905, ii, 706; from *Pharm. Zeit.*, 50, 621—622).—A criticism of Enell's process (see preceding abstract). The method in its present form only gives approximate results. L. DE K.

Bettendorff's Test for Arsenic. R. LOBELLO (*Chem. Centr.*, 1905, ii, 571; from *Boll. Chim. Farm.*, 44, 445—446).—The reagent is best prepared by adding one kilo. of hydrochloric acid of sp. gr. 1.19 to one kilo. of pure crystallised stannous chloride. After some time, the whole is diluted to two litres with acid of the same strength. On adding an equal volume of this solution to hydrochloric acid, the presence of even 0.001 per cent. of arsenious acid may be detected. Sulphuric acid may also be tested for arsenic by means of the tin solution. A comparative test with pure acids is advisable.

L. DE K.

Estimation of Arsenic in Toxicology. CARL MAI (*Zeit. Nahr. Genussm.*, 1905, 10, 290—292).—The finely-divided substance, such as the stomach, liver, intestines, muscular tissue, &c., is heated on the

water-bath to remove any alcohol if the latter has been used for preserving the substance, and is then treated with its own weight of fuming nitric acid containing 5 per cent. of sulphuric acid, the heating being continued until the whole mass becomes fluid. All the acid is now driven off by heating over a sand-bath and finally over a free flame. The resulting hard carbonaceous residue is powdered and distilled with from 5—6 times its weight of hydrochloric acid of sp. gr. 1.19. No reducing agent need be added and the whole of the arsenic will be found in the distillate when about one-third of the acid has distilled over. The distillate is evaporated after the addition of fuming nitric acid, and when almost dry a little sulphuric acid is added. The arsenic may then be estimated in the apparatus described previously by the author (*Abstr.*, 1905, ii, 284). W. P. S.

Separation of Arsenic from Vanadium and Molybdenum. CARL FRIEDHEIM, O. DECKER, and E. DIEM (*Zeit. anal. Chem.*, 1905, 44, 665—686).—Although trustworthy results may be obtained by several methods which are described, the following is to be preferred on account of its simplicity. About one gram of the arseno-vanadomolybdate is placed in a small flask together with 1.5 grams of potassium iodide and 70 c.c. of hydrochloric acid of sp. gr. 1.19. The mixture is distilled and the distillate evaporated with the constant addition of chlorine water, and the arsenic weighed either as the pentoxide or as magnesium pyroarsenate. The molybdenum and vanadium remaining in the flask may be separated by means of hydrogen sulphide. The precipitated molybdenum trisulphide is collected on a filter and weighed as the trioxide, whilst the vanadium in the filtrate is titrated with permanganate as usual. W. P. S.

The Turmeric Reaction for Boric Acid. ADOLF GOSKE (*Zeit. Nahr. Genussm.*, 1905, 10, 242—243).—It is stated that by dipping one end of a strip of turmeric paper in a solution containing boric acid and allowing the solution to ascend by capillary attraction, the test is rendered more sensitive than in the usual manner of testing. Even the smallest trace, such as 0.0001 per cent., of boric acid will give a brownish-red zone towards the upper part of the strip. W. P. S.

Detection of Boric Acid. OTTO MEZGER (*Zeit. Nahr. Genussm.*, 1905, 10, 243—245).—The following manner of carrying out the flame test is described. About 20 grams of the substance to be tested for boric acid are moistened with sodium carbonate solution, dried, and ignited. The ash is then treated with 20 c.c. of methyl alcohol and 2 c.c. of concentrated sulphuric acid and the mixture heated in a flask connected with a reflux apparatus. The heating is continued for fifteen minutes and the temperature not allowed to rise above 70°. After cooling, a stream of hydrogen is passed through the liquid and ignited as it leaves the flask. Very small quantities of boric acid may be detected in this way. The entire absence of water is of great importance as regards the sensitiveness of the test (compare *Abstr.*, 1905, ii, 480). W. P. S.

[Volumetric] Estimation of Boric Acid. ADOLF BEYTHIEN (*Zeit. Nahr. Genussm.*, 1905, 10, 283—286).—When using methyl-orange and phenolphthalein as indicators in the titration of boric acid, it is necessary to remove first any phosphoric acid which may be present. Each cubic centimetre of $N/1$ sodium hydroxide solution used then corresponds with 0.062 gram of boric acid. If phenolphthalein alone is employed as indicator, the removal of the phosphoric acid is unnecessary, but the quantity of boric acid neutralising 1 c.c. of $N/1$ sodium hydroxide varies with the concentration of the solution and the amount of boric acid present. The alkali solution should therefore be standardised against different amounts of boric acid. W. P. S.

Titration of Sodium Hydroxide in Presence of Sodium Carbonate. KARL NOVOTNY (*Zeit. Elektrochem.*, 1905, 11, 453—455).—When the carbonate is precipitated by exactly the required quantity of barium chloride and the sodium hydroxide then titrated by means of oxalic acid and phenolphthalein, the end-point is not sharp, the red colour continually returning until, after some days, enough acid has been added to saturate the carbonate as well as the hydroxide. This is due to the reaction between the solid barium carbonate and the dissolved sodium oxalate, and can be avoided either by using a considerable excess of barium chloride or by titrating with hydrochloric acid. T. E.

Estimation of Potassium Nitrate in Meats and Flesh Products. W. STÜBER (*Zeit. Nahr. Genussm.*, 1905, 10, 330—335).—A modification of Schlösing's method is described. The meat is boiled out with water and the extract evaporated to a small volume, after which it is transferred to a flask containing 20 c.c. of saturated ferrous chloride solution and 20 c.c. of 20 per cent. hydrochloric acid. The delivery tube of the flask is connected with the side-tube of an ordinary Schiff's nitrometer filled with boiled 20 per cent. sodium hydroxide solution. The nitrate solution is introduced drop by drop through a tapped funnel to the already boiling contents of the flask. The volume of gas obtained in the nitrometer is read off after the lapse of two hours and calculated into potassium nitrate, due notice being taken of the temperature and barometric pressure. The presence of organic nitrogenous substances is without influence on the results obtained. W. P. S.

Iodometric Determination of Aluminium in Aluminium Chloride and Aluminium Sulphate. SETH E. MOODY (*Amer. J. Sci.*, 1905, [iv], 20, 181—184).—The quantity of iodine liberated in Stock's process (Abstr., 1900, ii, 247 and 315) for the gravimetric estimation of aluminium is only about two-thirds of that required by the equation $\text{Al}_2(\text{SO}_4)_3 + 5\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{K}_2\text{SO}_4 + 3\text{I}_2$. If the iodine is removed by addition of sodium thiosulphate, further liberation of iodine takes place after a time, and this is accelerated by heating. The estimation of the liberated iodine can be employed as a means of determining aluminium if the iodide-iodate mixture is heated with the aluminium solution for 15—25 minutes in a Voit flask in a

current of hydrogen or steam, and the iodine liberated collected in the potassium iodide solution. The solution in the Voit flask as well as that in the receiver must be titrated. In the presence of ammonium salts, the process is not so accurate. Attempts to obtain a complete reaction by heating the mixture under pressure gave somewhat low results.

H. M. D.

Estimation of Manganese by means of Hydrogen Peroxide. EDUARD DONATH (*Zeit. anal. Chem.*, 1905, 44, 698—699).—The author claims that Zeller and he were the first to publish the method of separating manganese from other metals by means of hydrogen peroxide.

W. P. S.

Estimation of Manganese in Irons and Steels by the Persulphate Method. HANS RUBRICIUS (*Chem. Centr.*, 1905, ii, 709—710; from *Stahl. u. Eisen.*, 25, 890).—0.25 gram of steel drillings are dissolved in 25 c.c. of nitric acid of sp. gr. 1.2. The solution is boiled down to 12 c.c., 10 c.c. of *N*/10 silver nitrate are added, the whole is diluted to 300 c.c. and boiled with 10 c.c. of a 10 per cent. solution of ammonium persulphate. When cold, the manganese, which now exists as permanganate, is titrated with a solution containing 3 grams of arsenious acid and 9 grams of sodium hydrogen carbonate in 6 litres of water until a pure green colour is obtained. When testing iron drillings, 1 gram of the sample is dissolved in 60 c.c. of nitric acid of sp. gr. 1.2, boiled, and finally made up to 500 c.c., 50 c.c. (0.1 gram) are then mixed with 10 c.c. of *N*/10 silver nitrate diluted to 300 c.c. and boiled with 10 c.c. of a 5 per cent. solution of ammonium persulphate. The permanganate formed is then titrated with the above arsenical solution.

L. DE K.

Estimation of Manganese in the Presence of Chromium. MAX GRÖGER (*Chem. Zeit.*, 1905, 29, 987—988. Compare Abstr., 1904, ii, 392).—An application of Volhard's process of titrating manganous salts with permanganate after removal of any iron with zinc oxide. If chromium is present instead of iron, the process is conducted as follows: to the hot solution is added a sufficiency of an emulsion of zinc hydroxide (prepared by mixing 288 grams of crystallised zinc sulphate and 28 grams of pure potassium hydroxide with 500 c.c. of water) until the chromium is all precipitated. When cold, the liquid is diluted to, say, 250 c.c., and then filtered through a dry filter. Fifty c.c. are withdrawn, mixed with a solution of 20 grams of zinc sulphate in 150 c.c. of water, the whole is heated to boiling, and then titrated with permanganate. A second experiment should always be made.

L. DE K.

Use of Hydroxylamine in the Quantitative Analysis [Separation of Metals]. CARL FRIEDHEIM and PETER HASENCLEVER (*Zeit. anal. Chem.*, 1905, 44, 593—622).—From the results of their experiments, the authors conclude that the hydroxylamine method (Abstr., 1893, ii, 500) is of no use for the separation of iron from manganese and zinc, and that it compares unfavourably with the older and more

simple methods for separating iron from magnesium and copper. A double precipitation, at least, is necessary completely to separate aluminium from manganese, zinc, magnesium, and nickel, and the estimation of the metals in the filtrate is extremely difficult. Chromium may be separated from copper by this method, but in every other case untrustworthy results are obtained. Even where the method is applicable, it offers no advantages over the older processes.

W. P. S.

Electrolytic Analysis of Antimony. HERBERT DRAKE LAW and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1905, 1, 262—263).—Antimony can be estimated quantitatively if 5—7 grams of ammonium tartrate are added to 100 c.c. of the solution, and this is electrolysed with a current density of 0.2—1.0 ampere per sq. decm. and about 3 volts. The deposits from hot solutions (60—80°) adhere to the cathode very firmly. The colour of the deposit is improved by the addition of about 1 gram of tartaric acid to the solution. The antimony deposited from cold solutions is apt to be crystalline, unless very low current densities are employed and cannot be depended on.

H. M. D.

Ultimate Analysis of Organic Substances. HUGO HERMANN (*Zeit. anal. Chem.*, 1905, 44, 686—698).—From the analytical figures given, it is seen that good results may be obtained by absorbing the volatile constituents, such as sulphur, chlorine, iodine, &c., of organic compounds in suitable absorbent materials contained in small boats placed in a current of the combustion gas. Attention is drawn to the fact that the glass combustion tube and the substances in contact with the material being analysed may absorb sulphuric acid and halogens, and thus introduce errors into the results.

W. P. S.

Estimation of Carbon, Hydrogen, and Nitrogen in Cyanides. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1905, [iii], 33, 951—953. Compare Abstr., 1893, ii, 43).—For the estimation by combustion of carbon, hydrogen, and nitrogen in substances such as the cyanides, which burn completely only with difficulty, the author spreads the substance along the bottom of a platinum boat, 117 mm. long, 12 mm. broad, and 6.5 mm. deep, which is afterwards filled to the top with a mixture consisting of 83 parts of potassium dichromate and 13 parts of lead chromate. Details are given as to the size and filling of the combustion tube, the time required for combustion, and the volumes of air and carbon dioxide respectively passed through the tube. Analytical results obtained with potassium ferrocyanide show that this, after being dried at 120—125°, still retains 0.2 per cent. of water.

G. Y.

Coal Testing. OTTO PFEIFFER (*Chem. Centr.*, 1905, ii, 922—923; from *J. Gasbel*, 48, 713—715).—Only the volatile sulphur which passes into the gas need be estimated. The author prefers Hempel's method, in which 1 gram of the sample is burnt in oxygen in a closed bottle in presence of 20 c.c. *N*/10 alkali, the excess of the latter being

then titrated with *N*/10 sulphuric acid. It is necessary to test for and estimate traces of nitric and hydrochloric acids also formed during the combustion, and to calculate these into their corresponding quantity of sulphur, which must then be deducted.

L. DE K.

Estimation of Alcohol in Fusel Oil. R. PETERS (*Chem. Centr.*, 1905, ii, 573; from *Pharm. Centr.-H.*, 46, 563—568).—One hundred grams of the sample are mixed with 50 c.c. of light petroleum and the whole is shaken three times in succession with 100 c.c. of water. The aqueous solutions are united, a little charcoal is added, and 150 c.c. are distilled off. The distillate is mixed with 50 c.c. of light petroleum and shaken twice in succession with 100 c.c. of calcium chloride solution of sp. gr. 1.4. A little charcoal is added to the aqueous liquid and 100 grams are distilled off. The amount of alcohol contained therein is deduced from the sp. gr. as usual. In order to see more plainly the line of demarcation between the aqueous layer and the light petroleum, a trace of magenta may be added.

L. DE K.

Estimation of Higher Alcohols in Spirits. ERNST BECKMANN (*Zeit. Nahr. Genussm.*, 1905, 10, 143—152).—A modification of the author's original method (*Abstr.*, 1900, ii, 175) is described. Fifty c.c. of the spirit, previously diluted with water until it contains not more than 20 per cent. of alcohol by volume, are extracted with four successive quantities of 50 c.c. of carbon tetrachloride. Shaking for a few seconds each time is sufficient. The united extracts are washed twice with 20 c.c. of water and then agitated with 2 grams of potassium hydrogen sulphate and 1 gram of sodium nitrite. After removing the carbon tetrachloride, the residue is washed twice with a little carbon tetrachloride and the whole of the latter then shaken with about 20 c.c. of saturated sodium hydrogen carbonate solution to remove excess of nitrous acid. The carbon tetrachloride layer is now transferred to a separating funnel containing 75 c.c. of concentrated sulphuric acid, well shaken, and the mixture run slowly on to 150 grams of powdered ice. The resulting solution is finally titrated with permanganate solution. In order to obtain a sharp end-point in the titration, it is advisable to add about 20 per cent. of the permanganate solution in excess, and to titrate back with ferrous ammonium sulphate solution.

W. P. S.

Estimation of Glycerol in Wines. J. LABORDE (*Ann. Chim. anal.*, 1905, 10, 340—344).—From 50 to 100 c.c. of the wine are evaporated, and the syrup obtained is treated with 100 grams of finely divided lead and an alcoholic solution of slaked lime equal in quantity to the sugar present. The paste is well mixed with from 100 to 300 c.c. of alcohol and heated to a temperature of about 75°. After cooling, the whole is poured on a filter and a definite volume of the filtrate mixed with 0.5 gram of tartaric acid and a little lead and evaporated; the residue is then treated with calcium carbonate and extracted three or four times with the usual alcohol-ether mixture. The solution may be evaporated under reduced pressure and the glycerol weighed, or it may be acidified with a few drops of

ulphuric acid and the solvent evaporated off; 15 c.c. of water and 6 c.c. of sulphuric acid are then added and the mixture heated until the glycerol is completely carbonised. The flocculent carbon is now collected on a filter, dried, and weighed. W. P. S.

Estimation of Glycerol in Liqueur Wines. XAVIER ROCQUES (*Ann. Chim. anal.*, 1905, 10, 306—309).—Two hundred c.c. of the wine are evaporated to a syrupy consistency and the residue mixed with a quantity of calcium oxide equal to that of the sugars present in the volume of wine taken. After the lapse of half an hour, about 200 c.c. of 97 per cent. alcohol are added with constant stirring. The mixture, after a further half hour, is poured on a filter and the filter washed with alcohol. The filtrate is then acidified with an alcoholic solution of tartaric acid and most of the alcohol is distilled off. The residue is mixed in a basin with about 5 grams of calcium oxide and 10 grams of fine sand and dried in a desiccator under reduced pressure. The dry residue is treated in a flask with 80 c.c. of ethyl acetate and 20 c.c. of alcohol for two hours, then filtered, and a portion of the filtrate evaporated under reduced pressure over sulphuric acid for three days, when the residue of glycerol is weighed. W. P. S.

Comparative Estimations of Glycerol. FR. SCHULTZE (*Chem. Zeit.*, 1905, 29, 976—980).—A criticism of the various methods in use for the estimation of glycerol as applied to fats, soaps, and glycerol preparations. The conclusion arrived at is that the only trustworthy method is the hydriodic acid process proposed by Zeisel and Fanto.

L. DE K.

Nitrogenous Impurities of Glycerol and Fats. E. SCHMITT (*Chem. Centr.*, 1905, ii, 927; from *Les Corps Gras industriels*, 32, 20—21).—9.7 kilos. of a commercially pure glycerol were distilled with 500 c.c. of aqueous sodium hydroxide until half a litre had been collected. The alkaline distillate, which had a very pungent odour, was neutralised with hydrochloric acid and evaporated to dryness, when it yielded two grams of a semi-crystalline substance almost completely soluble in alcohol, and yielding crystals from that solvent. An analysis showed these to consist of salts of amines, carbylamines, and perhaps amidised derivatives, glycines, &c. These substances are no doubt decomposition products of proteid compounds present in the fats before saponification.

L. DE K.

Detection of Lævulose in the Human Body Fluids. RUDOLF OFNER (*Zeit. physiol. Chem.*, 1905, 45, 359—369).—The conclusion is drawn that the Seliwanoff reaction is always the best method for the detection of lævulose. The Neuberg-Strauss osazone method is not so satisfactory.

W. D. H.

Detection of Lævulose in the Presence of Glucosamine. CARL NEUBERG (*Zeit. physiol. Chem.*, 1905, 45, 500. Compare Abstr., 1903, i, 74; 1905, i, 90).—The mixture of the two substances is placed on the boiling water-bath with phenylmethylhydrazine for

three to five minutes; the phenylmethylosazone of lævulose is then formed and is precipitated on cooling. In this short time, the glucosamine does not form a compound.

W. D. H

Quantitative Hydrolysis of Saccharose, Maltose, Lactose, and Raffinose. BALTHASAR PFYL and BR. LINNE (*Zeit. Nahr. Genussm.*, 1905, 10, 104—110).—The authors employ a bronze pressure cylinder which is provided with a screw head carrying a manometer and valve chamber. Inside the cylinder there is a thick-walled glass tube, in which the solution of the sugar is placed. Any pressure up to 50 atmospheres can be obtained in the apparatus by connecting the valve chamber with a carbon dioxide cylinder. During the hydrolysis, the apparatus is suspended in a glycerol bath of the desired temperature. It was found to be impossible to completely hydrolyse saccharose in the presence of mineral or organic acids without destroying some of the products formed. In the absence of acids, however, saccharose is completely hydrolysed in $2\frac{3}{4}$ hours at a temperature of 125° and carbon dioxide pressure of 20 atmospheres. Dextrin, maltose, and lactose are not acted on under these conditions. Raffinose is quantitatively converted into melibiose and lævulose when heated for three hours at this temperature and pressure.

Maltose and lactose are best hydrolysed by heating in a 2 per cent. solution of benzenesulphonic acid for $2\frac{1}{2}$ hours at a temperature of 110° . The method may be used for the estimation of saccharose in honey, condensed milk, &c.

W. P. S.

Estimation of Sucrose in Presence of Lævulose and Dextrose. HENRI PELLET (*Chem. Centr.*, 1905, ii, 711—712; from *Bull. Assoc. Chim. Sucr. et Dist.*, 22, 1041—1048. Compare this vol., ii, 558).—The author has proved experimentally that the rotatory power of a solution of lævulose is increased by strong acids, but is not altered by sulphurous or acetic acid. Salts slightly increase the rotation. Prolonged heating considerably decreases the rotatory power in purely aqueous or saline solutions; addition of strong acids does not cause any alteration. It is therefore useless to acidify liquids containing sucrose before inverting according to Clerget's method. In cane-sugar molasses, the rotatory power of lævulose depends on the conditions under which the juice and the products obtained have been heated; the higher the temperature to which they have been subjected, the more is the rotatory power of the lævulose diminished. In the presence of dextrose, the action of the lævulose on polarised light may therefore be faint or strong. As the exact rotatory power of the lævulose contained in cane-sugar products which have been subjected to prolonged heating is not known, it is not possible to calculate the amount of lævulose and dextrose in a molasses, as the formula only applies to pure non-heated lævulose. This may also explain the untrustworthy action of the total reducing sugars often noticed in analyses of molasses.

L. DE K.

Two New Aldehyde Reactions. W. B. RAMSDEN (*Mem. Manchester Phil. Mag.*, 1905, 49, xvi, 1—3).—The first reaction may

be expressed by the equation $\text{Na}_2\text{SO}_3 + \text{H} \cdot \text{COH} + \text{H}_2\text{O} = \text{NaHSO}_3, \text{HCOH} + \text{NaOH}$. The test solution is made by dissolving 50 grams of sodium metabisulphite in 100 c.c. of water, adding 50 per cent. sodium hydroxide until nearly neutral, and finally decinormal alkali until phenolphthalein indicates the slightest alkalinity. If 2 c.c. of this solution and 1 c.c. of phenolphthalein are added to the neutralised solution to be examined, a pink to red colour is produced if formaldehyde is present. The delicacy of test is about four parts per million. Other aldehydes give the reaction, but not with the same dilution.

Nessler's reagent in fairly strong solutions of formaldehyde gives an immediate blackish-brown precipitate; in weaker solutions, a canary-yellow coloration is first produced; the solution then becomes slightly opalescent and darker in colour, and when kept a precipitate settles out. The reaction is quite apparent at a dilution of one part in two millions.

H. M. D.

The Hydrogen Peroxide Method of Estimating Formaldehyde. JOHN K. HAYWOOD and BERNARD H. SMITH (*J. Amer. Chem. Soc.*, 1905, 27, 1183—1188).—A study of the method proposed by Blank and Finkenbeiner. The following modification gives trustworthy results. Fifty c.c. of *N*-sodium hydroxide are placed in a 500 c.c. Erlenmeyer flask, and 50 c.c. of pure 3 per cent. hydrogen peroxide are added. Three c.c. of the sample are now added from a pipette, which almost reaches the liquid in the flask. A funnel is placed on the flask, which is then put on the steam-bath for five minutes. When cold, the excess of alkali is titrated with normal acid, using litmus as indicator. From the volume of the sample used and its sp. gr., the percentage by weight of formaldehyde may be calculated.

L. DE K.

Titration of Acetaldehyde. ALPHONSE SEYEWETZ and BARDIN (*Bull. Soc. chim.*, 1905, [iii], 33, 1000—1002. Compare *Compt. rend.*, 1905, 141, 959; Seyewetz and Gibello, *Abstr.*, 1904, ii, 521).—The solution is cooled to 4—5° and diluted until it contains not more than 7—8 per cent. of acetaldehyde. Of this solution, 10 c.c. are added to about 40 c.c. of a 10 per cent. solution of sodium sulphite containing a drop of a 0.2 per cent. phenolphthalein solution, and carefully neutralised by addition of an acid. The mixture is titrated with sulphuric acid, which is utilised according to the equation $2\text{Na}_2\text{SO}_3 + 2\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{SO}_4 = 2(\text{C}_2\text{H}_4\text{O}, \text{NaHSO}_3) + \text{Na}_2\text{SO}_4$. The reaction is not influenced by the presence of alcohol, paraldehyde, or acetal.

This method of estimation gives accurate results with even very dilute solutions of acetaldehyde (1 : 3000 aq.), as does also the method of estimating the aldehyde by titration of the hydrochloric acid liberated on its addition to hydroxylamine hydrochloride (compare Cambier and Brochet, *Abstr.*, 1895, i, 641).

G. Y.

The Vanillin Reaction for the Detection of Ketones. M. KUTSCHEROFF (*Zeit. anal. Chem.*, 1905, 44, 622—625).—The most satisfactory conditions under which this test (*Abstr.*, 1905, ii, 489) should be carried out are as follows: 3 c.c. of a freshly prepared 15 per

cent. solution of vanillin in pure alcohol are added to the solution to be tested, and then 1 c.c. of concentrated sulphuric acid is introduced. After fifteen minutes, the coloration, if any, is observed. Acetone, when present in quantity greater than 0.01 per cent., gives a carmine-red coloration, whilst the higher ketones yield a blue or greenish-blue colour. On diluting the mixture with twice its volume of water, the red coloration changes to yellow, but the blue remains unchanged. Should both acetone and higher ketones be present, the colour produced on dilution will be more or less green. Aldehydes, if present, should be removed by fractional distillation before applying the test.

W. P. S.

Electrometric Determination of the Acidity of Urine. LADISLAUS VON ROHRER (*Pflüger's Archiv*, 1905, 109, 391—392. Compare Abstr., 1901, ii, 672).—A reply to H. Sahli (*Lehrbuch Klin. Untersuchungsmethoden*, 1905). The author has already drawn attention to the difference between the expressions hydrion concentration and acidity as determined by titration with alkali. J. J. S.

Estimation of the Volatile Fatty Acids in Palm Oils and Butter. ORLA JENSEN (*Zeit. Nahr. Genussm.*, 1905, 10, 265—283).—The author has separated the volatile fatty acids found in cocoa-nut oil and butter by fractional precipitation of their silver salts, and has determined the solubilities of these acids in water. Capric [decoic] acid is practically insoluble in water at a temperature of 15°, whilst caprylic [octoic] acid and caproic [hexoic] acid dissolve to the extent of 0.079 and 0.872 per cent. respectively. Analyses of butter from various countries are given, the results showing that the percentages of butyric and caproic acids in butter vary very considerably. In mixtures containing known quantities of butter and cocoa-nut oil it is shown that the Reichert-Meissl and Polenske values are always higher than the calculated values, but that the Kirschner values (Abstr., 1905, ii, 213) of the mixtures agree well with the calculated figures. The results obtained in Kirschner's process vary in proportion to the Reichert-Meissl values and this process is of more use in detecting the presence of butter and cocoa-nut oil in margarine than for estimating cocoa-nut oil in butter. W. P. S.

Valuation of Tannic Acid. WALTER S. WILLIAMS (*J. Soc. Chem. Ind.*, 1905, 24, 877—879).—The well-known process of titration with permanganate in the presence of sufficient indigo solution is recommended and the operation is repeated after removing the true tannin from the solution by means of gelatin.

A practical printing experiment on a small scale is recommended as being sufficiently accurate for the wants of dyers in order to form an opinion as to the mordanting power of their tannins.

Dreaper's statement that gallic acid is equally suitable from a dyer's point of view seems to be erroneous. L. DE K.

[The Amount of Fat in] Goats' Milk. UJHELYI (*Milch.-Zeit.*, 1905, 34, 403—405).—Systematic analyses of the milk yielded by

seven goats during the year 1904 showed the average amount of fat to be 4.01 per cent. This amount is lower than that usually found in goats' milk when the animals are fully matured and in good condition, but these goats were well kept. W. P. S.

Estimation of Fat in Milk deficient in Fat. TH. SV. THOMSEN (*Landw. Versuchs-Stat.*, 1905, 62, 387—399).—When the proteids of milk are peptonised and the milk dried with a mixture of kaolin and barium carbonate for the estimation of fat, the same results are obtained with Gottlieb's method as with the extraction method. The results agree, moreover, with those obtained by Gottlieb's method with unpeptonised milk, but are considerably higher than the results obtained in unpeptonised milk by the extraction-method.

It is shown that the amount of insoluble residue obtained in Gottlieb's method is insignificant, and that it dissolves completely in a mixture containing less ether and more light petroleum.

N. H. J. M.

Estimation of Fat, Lactose, and Proteids in Milk. THEODOR LOHNSTEIN (*Chem. Centr.*, 1905, ii, 353; from *Ber. deut. pharm. Ges.*, 15, 98—107).—The estimation of fat in milk is made by means of the author's galactoliptometer (*Chem. Centr.*, 1905, i, 1334). For the estimation of the lactose, 5 c.c. of the milk are mixed in a test-tube with 0.4 c.c. of 25 per cent. hydrochloric acid, and heated for thirty minutes in a boiling brine-bath. The solution is cooled rapidly, and, after adding 1 c.c. of 15 per cent. potassium hydroxide, is diluted to 10 c.c. Without removing the curd, the whole is fermented for 2—2½ hours at 32—38° in the fermentation saccharometer, when all the dextrose disappears before the galactose begins to ferment. The result multiplied by 4.33 represents the lactose.

The proteids (*e*) are calculated from the sp. gr., the fat, and the lactose. For cow's milk, the formula is

$$e = \frac{d - dw}{0.0028} - 2.29 - 1.34z + 0.277f,$$

in which *d* = sp. gr. at 4°/4°, *dw* the sp. gr. of water at the temperature of the experiment, *z* the lactose, and *f* the fat. In the case of human milk, 1.2 is substituted in the formula for 2.29. L. DE K.

Variations in the Non-fatty Solids of Milk Resulting from Interrupted Milking. FRANZ LAUTERWALD (*Milchw. Zentr.*, 1905, 1, 385—400).—Results are given of analyses of various fractions of milk obtained from a number of cows, from which it is seen that the percentage of non-fatty solids decreases as the milking proceeds, whilst the amount of fat in the fractions gradually increases (compare *Abstr.*, 1902, ii, 466). When, however, the non-fatty solids are calculated on the fat-free serum, the variation in the percentage practically disappears, showing that the depression of the non-fatty solids in the later fractions of the milk is balanced by the increase of fat and, further, that the formation of fresh milk in the udder does not take place to any great extent during the milking. W. P. S.

Analysis of Curdled Milk. LUDWIG VON WISSELL (*Milchw. Zentr.*, 1905, 1, 401—417).—The addition of ammonia to sour or curdled milk in order to render the latter liquid again has no influence on the estimation of the fat in the milk by Gottlieb's, Gerber's, or the plaster methods if the quantity of ammonia added is allowed for. The calculated sp. gr. of the sample, however, is usually about 0.0010 too high, and the total solids are on the average 0.44 per cent. too low.

W. P. S.

Estimation of Fat in Butter by Gottlieb's Method. ANTON BURR (*Zeit. Nahr. Genussm.*, 1905, 10, 286—290).—From 1 to 1.3 grams of the well-mixed sample are washed through a funnel into a Röse's cylinder by means of about 10 c.c. of hot water. After cooling, 1 c.c. of ammonia is added, then 10 c.c. of alcohol, and finally 25 c.c. of ether. The alcohol and ether are poured through the funnel to wash all the adherent fat into the cylinder. The remainder of the process is carried out as in Gottlieb's method for the estimation of fat in milk (*Abstr.*, 1905, ii, 559).

W. P. S.

Detection of Rancidity in Butter. PAUL SOLTSIEN (*Chem. Rev. Fett-Harz-Ind.*, 1905, 12, 177—178).—Although the smell of rancid butter is unmistakable, it is advantageous to confirm this by means of a chemical reaction. For the latter purpose, the butter is distilled in a current of steam, the distillate is neutralised and again distilled. This second distillate is then mixed with Welmans' reagent (*Abstr.*, 1900, ii, 697) and the mixture treated with an excess of ammonia. After the lapse of about one minute, a blue coloration appears if the fat is rancid. The depth of colour obtained depends on the degree of rancidity.

W. P. S.

Estimation of Fat. LEO LIEBERMANN (*Pflüger's Archiv*, 1905, 108, 481—488).—The author replies to various criticisms of his method of fat estimation (*Abstr.*, 1898, ii, 655). He states that concentrated potassium hydroxide does not act on fat-free peptones, albumins, or cellulose to produce decomposition products soluble in ether. He further states that although his method gives higher results than the extraction method under the usual conditions, yet the latter agrees with the former if the extraction with alcohol is prolonged for about a day, and similarly with ether. A complete extraction of the fat is effected with difficulty.

J. J. S.

Iodine Numbers of Oils. RAFFAELLO PAJETTA (*Gazzetta*, 1905, 35, ii, 53—57).—In order to ascertain the effect of age on the value of the Hübl's iodine number of an oil, the author has determined, for fresh and old samples of cod-liver and olive oils, the iodine numbers for: (1) the oils themselves; (2) the oils after being rendered neutral by washing with alcohol, and (3) the alcoholic washings. The mean values obtained are given in the following table:

	Original oil.	Neutral oil.	Alcoholic washings.	Solubility of original oil in 1000 c.c. of alcohol.
Cod liver oil, fresh	137.6	136.3	143.6	37.2 grams
„ „ of 1901.....	146.0	142.7	155.3	26.9 „
Olive oil, of 1903	82.78	81.19	84.84	25.15 „
„ „ very old and discoloured.	68.89	67.99	69.05	70.9 „

The numbers obtained for the neutral oil indicate the quantities of iodine absorbed by the fixed combined acids (which are almost insoluble in alcohol), that is, by the mixture of glycerides forming the basis of the oil. Those given by the alcoholic washings represent the iodine absorbed by the free acids and by the aldehydic and ketonic products developed as the oil becomes rancid.

It will be seen from the above table that the iodine number of the oil is roughly the mean of those of the neutral oil and the alcoholic extract. With increase of rancidity, the difference between these two outside values diminishes considerably, the three numbers tending, in the case of olive oil, to become equal. For different samples of any one oil, the iodine numbers of the neutral oils are more nearly equal than those of the original samples. T. H. P.

Test for the Purity of Cocoa-nut Oil. ERNEST MILLIAU (*Ann. Chim. anal.*, 1905, 10, 298—302).—Four c.c. of the filtered oil are mixed in a test-tube with 2 c.c. of a saturated solution of phloroglucinol in ether and 2 c.c. of a saturated solution of resorcinol in benzene. After cooling the mixture to a temperature of 10°, 4 c.c. of nitric acid of sp. gr. 1.38 are added and the whole shaken for five seconds. Pure cocoa-nut oil remains quite unchanged, but the presence of any seed oil, such as cotton, sesamé, arachis, rape, &c., causes a distinct currant-red coloration to appear. As little as 5 per cent. of seed oil may thus be detected. Colorations which appear subsequently are to be disregarded. W. P. S.

Copal Oils. LEO SCHMOELLING (*Chem. Zeit.*, 1905, 29, 955—956).—A series of experiments made to distinguish the Kauri oil from the Manilla variety. The following table, which relates to the crude oils, is of interest:

	Kauri oil.	Manilla oil.
Acid number	3.0	28.3
Cold saponification number	4.9	45.7
Ester number	1.9	17.4
(Waller's) Iodine number	288.9	230.4

The iodine numbers are, however, much increased on distillation in steam. For further particulars, the original paper should be consulted.

L. DE K.

Sesamé Oil. H. SPRINKMEYER and H. WAGNER (*Zeit. Nahr. Genussm.*, 1905, 10, 347—353).—Results of analyses of samples of Indian, Levantine, and African sesamé oils show that there is little difference between the cold and hot pressed oils. The African oil

yielded constants which differed considerably from those given by the other two varieties. For instance, the iodine value was 114, the refraction at 40°, 60.6, and the polarisation +1.42°. The following percentages of oil were yielded by the seeds: Indian, 49.76; Levantine, 50.14; African, 54.14.

For detecting small quantities of sesamé oil in butter and margarine, the author recommends extracting the substances which give the coloration with Baudouin's reagent by means of glacial acetic acid. The residue obtained on evaporating the acid extract is treated with a little barium hydroxide and again evaporated. Artificial colouring matters in the butter remain insoluble with the barium soaps when the residue is extracted with light petroleum, but the substances giving Baudouin's reaction are dissolved. The petroleum extract is finally evaporated and the residue tested as usual. W. P. S.

Veronal. EMIL FISCHER and J. VON MERING (*Chem. Centr.*, 1905, ii, 640—641; from *Die Therapie der Gegenwart.*, 1904, 45. Compare Abstr., 1903, i, 552).—Veronal (diethylmalonylcarbamide) is determined in urine in the following manner. The urine is reduced by distillation under diminished pressure to about one-fifteenth its original volume and extracted with ether. The residue from the ethereal solution is boiled with animal charcoal for half an hour, filtered, and cooled to 0°, when the veronal separates in colourless needles melting at 191° (corr.).

After the consumption of 4 grams of veronal in two days, 2.49 grams (62 per cent.) was recovered in the urine of five days. The elimination was, however, not complete in that time and the method is not absolutely quantitative. N. H. J. M.

Estimation of Uric Acid and of Purine Bases in Human Urine. MARTIN KRÜGER and JULIUS SCHMID (*Zeit. physiol. Chem.*, 1905, 45, 1—13. Compare Krüger and Wulff, Abstr., 1895, ii, 94; Krüger, *ibid.*, 1896, ii, 281; Salkowski, *ibid.*, 1898, ii, 269; Huppert, *ibid.*, 1897, ii, 293).—The Krüger-Wulff method of precipitation with copper sulphate and sodium hydrogen sulphite has been employed for uric acid and the following pure purine bases which occur in urine: xanthine, 1-methyl- and 7-methyl- and 1:7-dimethyl-xanthines; guanine, 7-methylguanine, adenine, and hypoxanthine. The results indicate that all these compounds are completely precipitated by the original Krüger-Wulff method, or more quickly by boiling for three minutes, and that the presence of sodium chloride or sodium chloride and acetate does not affect the completeness of the precipitation.

Estimations of paraxanthine by the ammoniacal silver method give low results, as the silver compound is appreciably soluble in ammonia.

In the estimation of uric acid, the copper precipitate as obtained above is decomposed with sodium sulphide, acidified with hydrochloric acid, evaporated, and kept for several hours. A Kjeldahl determination is made of the uric acid deposited.

Krüger and Schmidt's method (Abstr., 1900, ii, 31) for the estimation of purine bases in presence of uric acid gives good results. Acids,

very dilute alkalis, and manganese dioxide do not appreciably affect the bases. J. J. S.

Meconic Acid in the U.S.P. Opium Assay and Certain Meconates. EDWARD MALLINCKRODT, jun., and EDWARD A. DUNLAP (*J. Amer. Chem. Soc.*, 1905, 27, 946—964).—When assaying opium by the U.S.P. (1890) process, a yellow, scaly coating is observed on the bottom of the flasks which evidently is not morphine. The authors find it to be a double salt of meconic acid with calcium and ammonium, $\text{CaNH}_4\text{C}_7\text{HO}_7 \cdot 2(3)\text{H}_2\text{O}$, and its importance in the assay process lies in the fact that, when the morphine is finally found by titration, this compound consumes nearly a quarter as much acid as the morphine itself, and so more or less vitiates the results.

Contrary to previous statements, it is found that both di- and tri-barium meconates are practically insoluble in barium hydroxide solutions. An attempt to prepare the mono-meconate failed, as the di-meconate was deposited, leaving free meconic acid in the mother liquor. L. DE K.

Alkaloid Reactions (Amorphous Aconitine). C. REICHARD (*Chem. Centr.*, 1905, ii, 357—358; from *Pharm. Centr.-H.*, 46, 479—486. Compare this vol., ii, 563).—In applying the phosphoric acid test, metaphosphoric acid may be substituted for the ortho-acid. Aconitine added to a concentrated acid solution of antimony trichloride gives a dark or black coloration. If a clear, minute crystal of potassium ferrocyanide is added to a drop of sulphuric acid in which has been dissolved aconitine and a little sodium ortho-arsenate, it turns blue after a few minutes. If no arsenate has been added, a blue colour is also noticed, but it then soon fades. Concentrated sulphuric acid gradually dissolves aconitine to a clear, bright yellow solution, which on warming becomes a dark violet-brown. A mixture of aconitine and ammonium molybdate becomes blue when moistened with sulphuric acid; potassium dichromate similarly gives a fine dark green coloration. If now a few particles of ammonium persulphate are added and a gentle heat is applied, the blue colour changes to a bright yellow and the green to a blue or bluish-green. Mercuric chloride has no action, but mercurous nitrate yields at once a black precipitate with aconitine. The alkaloid dissolves in concentrated nitric acid to an almost colourless solution. A mixture of aconitine, ammonium persulphate, and sulphuric acid, when gently heated, first turns a deep brownish-black, but after a few minutes becomes quite colourless and emits an odour of ozone. Copper sulphate and copper oxychloride are not reduced by aconitine, and iodine is not liberated from potassium iodate in presence of sulphuric acid. Aconitine has no action on ferric chloride, but on evaporating the mixture and moistening the residue with sulphuric acid, a dark brown solution is obtained. L. DE K.

Estimation of Arginine with Permanganate. GUSTAV ORGLMEISTER (*Beitr. chem. Physiol. Path.*, 1905, 7, 21—30. Compare Pommerrenig, *Abstr.*, 1902, ii, 274; Kutscher and Zickgraf, 1903, i, 666; Zickgraf, 1904, i, 462).—Pommerrenig's negative results

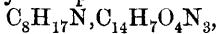
were largely due to the use of cold potassium permanganate instead of a solution of the hot calcium salt, and in using picric acid as a precipitating agent for guanidine. To estimate the arginine groups in albumin this is first hydrolysed with sulphuric acid, then oxidised with calcium permanganate by the Kutscher-Zickgraf method, and the guanidine thus obtained estimated either by weighing the guanidine picrate obtained by the addition of sodium picrate solution, or by estimating the nitrogen in it.

The percentages of arginine have been determined in a number of proteids by this method. J. J. S.

Estimation of Alkaloids in Coca Leaves. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1905, [ii], 24, 307—308).—A modification of Keller's method for the estimation of the alkaloids in coca leaves.

M. A. W.

Reactions for distinguishing between Nicotine and Cicutine. R. TORRESE (*Chem. Centr.*, 1905, ii, 416; from *Giorn. R. Accad. Med. Torino*, 1905, 10).—The method of distinguishing between these two substances is based on the difference in crystalline form of their compounds with 4-piperonyl-3:5-dicyanoglutaconimide and 4-isobutyl-, 4-phenyl-, and 4-hexyl-3:5-dicyanohydroxypyridine respectively. This distinction is most characteristic in the case of the piperonyl compounds. The piperonyl compound of nicotine is obtained as a gelatinous precipitate which, after 20—24 hours, becomes crystalline; after recrystallising from water, it forms long, thin, transparent prisms. The corresponding piperonyl compound of cicutine,



forms short, flat prisms, which turn red at 247° and melt at 252° ; they are soluble in boiling water, slightly soluble in cold water and hot alcohol, but insoluble in boiling ether. The isobutyl compound gives no precipitate with cicutine hydrochloride, whereas with nicotine it forms a compound of the formula $2\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3, \text{C}_{10}\text{H}_{14}\text{N}_2$, forming star-shaped aggregates of long, transparent crystals which darken at 180 — 200° and char at 270° . The hexyl compound gives with nicotine stellar aggregates of prismatic crystals, whilst with cicutine it forms, after 10—12 hours, small plates. The phenyl compound gives fan-shaped aggregates of long prisms with nicotine and thick plates with cicutine. It is possible by means of these differences in crystalline form to identify both alkaloids in a Stas-Otto extract, provided the solution is free from salts of the alkali metals or metals of the alkaline earths. Aniline and sparteine also give precipitates with the piperonyl reagent. The paper contains tables showing the limit of dilution at which nicotine and cicutine are precipitated by the four reagents as well as by a number of the ordinary alkaloidal reagents.

P. H.

Estimation of Pyramidone. A. ASTRUC and G. PÉGURIER (*Ann. Chim. anal.*, 1905, 10, 302—303).—An aqueous solution of the pyramidone is treated with an excess of picric acid solution of known strength. After shaking for a few minutes, the precipitate is collected

on a filter, and the excess of picric acid titrated in the filtrate with *N*/10 sodium hydroxide solution, using phenolphthalein as indicator. One molecule (231) of pyramidone precipitates one molecule of picric acid (229).
W. P. S.

Separation of Strychnine and Brucine. D. LLOYD HOWARD (*Analyst*, 1905, 30, 261—263).—The author has investigated Keller's method for the separation of strychnine from brucine (Abstr., 1903, ii, 342) and finds that at a sufficiently low temperature brucine can be completely destroyed in the presence of strychnine without injury to the latter. The temperature at which the treatment with nitric acid is carried out should be as near 0° as possible. The defects of Keller's method are shown to be simply those attendant on the use of a mixture of chloroform and ether as a solvent. Gordin's statement (*loc. cit.*) that the above method gives results about 4 per cent. too low, is not borne out by the author's experiments.

W. P. S.

Colorimetric Estimation of Thiophen. CARL SCHWALBE (*Chem. Zeit.*, 1905, 29, 895—896. Compare Abstr., 1904, i, 337).—The author estimates thiophen in crude benzenes by adding 1 c.c. of the sample to a mixture of 25 c.c. of sulphuric acid and 25 c.c. of isatin-sulphuric acid (0.5 gram of isatin in 1000 grams of pure sulphuric acid). After thorough shaking, the green colour of the mixture is compared with that obtained in another experiment with a pure benzene to which a definite amount of thiophen has been added. The process is no longer applicable when the percentage of thiophen falls below 0.05.

L. DE K.

Evaluation of Aloes. LEOPOLD VAN ITALLIE (*Pharm. Weekblad*, 1905, 42, 553—560).—The author states that Curaçoa aloes are from a pharmaceutical point of view not in the least inferior to the Cape variety, although they give a reaction for *isobarbaloin*. They are rich in aloin, but rather poor in substances which on treatment with nitric acid yield chrysamic acid. The reaction with nitric acid, however, gives rise to several by-products and is not a quantitative one.

After a futile attempt to estimate the amount of aloin by taking advantage of the green fluorescence which occurs on treating aqueous aloe solution with borax, the author endeavoured to apply the reaction with bromine both volumetrically and gravimetrically, but although very satisfactory results were obtained with pure aloin the process failed with aloes. A method based on the acetylation of aloin failed altogether with aloes, as the end reaction in the final titration could not be observed.

The following process for the estimation of the non-resinous matters, which is a slight modification of the method proposed by Tschirch and Hoffbauer, is recommended. Five grams of the powdered sample are heated in a 50 c.c. flask with 5 c.c. of methyl alcohol until a homogeneous liquid is obtained. When cooled to 60°, 30 c.c. of chloroform are gradually added with vigorous shaking for five minutes. After some time the chloroform may be poured off quite clear. The time may be shortened by placing the flask in cold water. After expelling the chloroform from the residue, this is again treated

with 5 c.c. of methyl alcohol and 30 c.c. of chloroform, and this operation is repeated three times. The undissolved resin should then no longer be sticky but form a powder. The mixed chloroform extracts are then freed from chloroform by distillation, and the residue is finally dried at 100° and weighed.

Two samples of Cape aloes yielded respectively 82 and 56.2 per cent. of extract; three samples of Curaçoa aloes gave respectively 86.4—88.6 and 78.3, and a sample of Aruba aloes gave 61.04 per cent. The figures given are the mean of two determinations in each case.

L. DE K.

Influence of Bran on the Estimation of Gluten and on the Suitability of Flour for Bread-making. LÉON LINDET and LOUIS AMMANN (*Compt. rend.*, 1905, 141, 56—58).—The quantitative separation of gluten from flour becomes the more difficult as the latter decreases in quality. In the case of flours known to the trade as “thirds” and “fourths,” it is practically impossible to obtain a coherent mass of gluten. This is due to (1) the abnormal acidity of inferior flour; (2) the increased proportion of glutenin to gluten; (3) the presence of a mucilaginous substance; and (4) the particles of cellular tissue which interfere with the adhesive properties of the gluten. It has been noted that gluten obtained from inferior flours contains less nitrogen than that yielded by best wheat-flour, but this is accounted for by the fact that the cellular tissue (bran) is separated together with the gluten. On account of its feeble cohesive property, flour containing much bran “rises” unsatisfactorily when used for bread-making. W. P. S.

Volhard's Titrimetric Method for the Estimation of Pepsin and Trypsin. WALTER LÖHLEIN (*Beitr. chem. Physiol. Path.*, 1905, 7, 120—143).—The method of estimating pepsin is based on the fact that unaltered casein dissolved in the fermenting liquid containing hydrochloric acid is completely precipitated by sodium sulphate, and the increase in the acidity of the filtrate as determined by titration, using phenolphthalein as indicator, is a measure of the extent to which the peptic digestion has proceeded. A study of numerous experiments shows that the Schütz-Huppert time and fermentation laws hold good, the increase in acidity being proportional to the square root of the product of amount of ferment and time. These laws no longer hold when the product of ferment (in c.c.) and time (in hours) is greater than 16. The equation $x = v^2/ft$, gives the number of units of pepsin present (compare this vol., ii, 732).

The estimation of trypsin in pancreatin may be conducted in a similar manner. The casein solution is mixed with pancreatin to which a little alkali has been added, and the mixture kept at 40° for a given length of time. *N*-Hydrochloric acid and 20 per cent. sodium sulphate are then added, the precipitated casein removed, and the increase in acidity of the filtrate determined.

The results show that the extent of fermentation is directly proportional to the amount of ferment solution and to the time, or that the number of units of ferment may be calculated from the formula $x = v/ft$. It is shown that normal stomach juices contain no trypsin.

J J. S

General and Physical Chemistry.

Development of Spectro-chemistry. JULIUS W. BRÜHL (*Royal Institution Lecture*, May 26, 1905).—An historical survey of the work done up to the present time on specific and molecular refraction.

J. C. P.

Refractive Index of Gaseous Fluorine. CLIVE CUTHBERTSON and E. B. R. PRIDEAUX (*Phil. Trans.*, 1905, 205 A, 319—331).—In the earlier measurements of the refractive index, in which a current of electrolytic fluorine was passed through a hollow copper prism provided with fluorspar apertures until a steady state was reached, concordant values could not be obtained. The chief causes of this are now found to be that the air cannot be completely displaced from the measuring apparatus, and that the electrolytic fluorine prepared by Moissan's method contains oxygen and ozone. These sources of error have now been taken into account. The electrolytic fluorine, after passing through a long platinum spiral cooled to -78° to remove hydrogen fluoride, and through a second spiral heated at $250-300^{\circ}$ to destroy ozone, entered the Jamin refractometer tube, which was made of platinum-iridium with end-plates of fluorspar. After the measurement of the refractivity, the proportions of fluorine, oxygen, and nitrogen in the tube were determined, the fluorine being conveniently absorbed by lead. The corrected mean value of the refractive index of gaseous fluorine is 1.000195. This value makes the ratio of the refractivities of fluorine and chlorine almost exactly 1:4, which is the ratio that the refractivities of nitrogen, oxygen, and neon bear to phosphorus, sulphur, and argon respectively (compare *Abstr.*, 1905, ii, 129).

H. M. D.

Refractive Indices of Sulphuric Acid at Different Concentrations. VICTOR H. VELEY and JOHN J. MANLEY (*Proc. Roy. Soc.*, 1905, A, 76, 469—487).—The refractive indices of sulphuric acid solutions containing from rather under 1 per cent. to rather more than 99 per cent. have been determined for the four lines H_{α} , D , H , and H_{γ} . The temperature-coefficients have been measured and used for reducing all observations to 15° . The maximum values of the refractive indices and of the first constant of Cauchy's formula occur at a point corresponding approximately with the composition of the hydrate, $H_2SO_4 \cdot H_2O$; any indication of the existence of other hydrates is doubtful; Lorentz's expression, $(\mu^2 - 1)/(\mu^2 + 2)d$, is a linear function of the percentage up to 90 per cent. The refractive indices, the Cauchy constants, and the Lorentz expression all show irregularities for concentrations between 92 and 100 per cent.; these irregularities are consistent among themselves, as also with a maximum density at about 97 per cent., and a minimum point between 99 and 100 per cent.

J. C. P.

Spectrum of Silicon; Spectrum of Fluorine. JOSEPH LUNT (*Proc. Roy. Soc.*, 1905, *A*, 76, 118—126).—Of the lines λ 4089.1, λ 4096.9, and λ 4116.4, attributed by Lockyer to silicon (see Lockyer and Baxandall, this vol., ii, 129), the author finds only the first and third really to be due to that element. He supplements what is regarded as the insufficient evidence brought forward by Lockyer and Baxandall in support of their conclusions. Two new low temperature silicon lines are recorded, namely, λ 4191.0 and λ 4198.5.

A list of lines ascribed to fluorine is appended. The strongest of these are λ 4103.6, λ 4109.3, λ 4246.5, λ 4299.3, and λ 4446.8.

J. C. P.

Enhanced Lines. JACOB STEINHAUSEN (*Chem. Centr.*, 1905, ii, 1073; from *Zeit. wiss. Photographie, Photophysik u. Photochemie*, 3, 45—48).—Lockyer's "enhanced lines" or those lines which occur in spark spectra, but are either very much less marked or entirely absent in arc spectra, have been examined in the case of aluminium, antimony, lead, cadmium, magnesium, mercury, bismuth, tin, zinc, barium, calcium, strontium, and tellurium. An induction apparatus which was capable of giving a spark of 100 cm. was used, and both the spark and the arc spectra were photographed on the same plate by means of a concave grating of a curvature corresponding with 1 metre radius. The intensity of the lines was estimated and values ascribed to each ranging from 10 to 1. A tabular list of the enhanced lines is given in the original paper. The intensity of the lines of the spark spectra was usually greatest at the ends of the spark and least in the middle; exceptions were found, however, in the ultra-violet. The spectrum of sparks passing between electrodes of aluminium and tin showed the lines of tin at both electrodes; the lines must therefore be caused by the vapour of the metal. It is probable that the phenomenon of enhanced lines does not only depend on rise of temperature, but also on increase of dissociation.

E. W. W.

Absorption Spectra of Vapours. WILHELM FRIEDERICHSEN (*Chem. Centr.*, 1905, ii, 1073—1074; from *Zeit. wiss. Photographie, Photophysik u. Photochemie*, 3, 154—164).—The absorption spectra of iodine, tellurium dichloride, and manganese perchloride, Mn_2Cl_7 , have been examined. An Auer lamp was used for illumination, and the spectra, which were of low dispersion (4 cm.), were photographed. The iodine vapour was contained in quartz vessels which could be heated to 920°. At low temperatures, the vapour gave a good absorption band spectrum, and on heating the absorption increased up to 500°, but at temperatures above this it again rapidly decreased; at the maximum temperature, the absorption bands entirely disappeared. It is concluded that the vapour which shows the band spectrum consists of diatomic molecules. The absorption bands of the spectra of tellurium dichloride and manganese perchloride were found to be arranged in groups.

The ultra-violet absorption spectrum of benzene was also examined, the source of illumination being in this case a luminous capillary filled

with hydrogen (Schumann's method), closed on one side by a quartz plate. The spectrum beyond λ 2694 contained eight distinct groups of bands. A comparison with Hartley's results (Trans., 1898, 73, 695) showed that the whole of the bands had moved towards the red end, and the smaller the wave-length the greater had been the displacement.

E. W. W.

Ultra-violet Absorption Spectra of the Purines. CHARLES DHÉRE (*Compt. rend.*, 1905, 141, 719—721).—Using as a source of illumination the electric spark between electrodes of iron and Eder's alloy (cadmium, zinc, and lead in equal parts), the author has photographed the absorption spectra afforded by different thicknesses of solutions of some members of the purine series. The longest wave-length transmitted through (1) a thickness of 20 mm. of a solution (1 in 10,000) of hypoxanthine (6-oxypurine) is 274.8, (2) a thickness of 40 mm. of a solution (1 in 20,000) of xanthine (2:6-dioxypurine) is 287.2, and (3) a thickness of 60 mm. of a solution (1 in 40,000) of uric acid (2:6:8-trioxypurine) is 306.0. These results show that the absorption spectra of the three purines extend towards the least refrangible end of the spectrum as the proportion of oxygen in the molecule increases.

M. A. W.

Phosphorescent Spectra of S δ and Europium. Sir WILLIAM CROOKES (*Proc. Roy. Soc.*, 1905, A, 76, 411—414).—The strong line in the phosphorescent spectrum of europia is not coincident with the old anomalous line (compare Demarçay, Abstr., 1901, ii, 511), the wave-length of the europia line being λ 6128, and that of S δ λ 6094. The S δ line is developed brilliantly when a little europia is added to a mixture of yttria and samaria.

J. C. P.

Colours in Metal Glasses, in Metallic Films, and in Metallic Solutions. II. J. C. MAXWELL GARNETT (*Phil. Trans.*, 1905, A, 205, 237—288).—In this paper, mathematical analysis is applied to the explanation and co-ordination of the colours exhibited by certain metals in different circumstances. One of the conclusions reached is that Carey Lea's silver is not allotropic, but consists of normal silver in a finely-divided state. A similar view is adopted by the author regarding other so-called allotropic forms of metals.

J. C. P.

Investigation of Fluorescence. HUGO KAUFFMANN (*Chem. Zeit.*, 1905, 29, 1032—1034).—A survey of recent researches on fluorescence.

J. C. P.

Fluorescence of Sodium Vapour and the Resonance Radiation of Electrons. ROBERT W. WOOD (*Phil. Mag.*, 1905, [vi], 10, 513—525. Compare Abstr., 1903, ii, 621).—The author has succeeded in detecting the lateral emission of yellow light by non-luminous sodium vapour when illuminated by the light from a very intense sodium flame.

The same phenomenon has been observed in the region of the

channelled absorption, but in this case radiations of other wave-lengths are emitted as well as that of the exciting light. The phenomenon is termed *resonance radiation* to distinguish it, if need be, from fluorescence.

The apparatus employed consisted of a seamless steel tube, 3" diameter, 30" long, fitted with plate-glass ends. This tube could be exhausted, and inside it, at its centre, was placed a smaller steel tube in which the sodium was contained. The ends of the smaller tube were closed by steel discs provided with oval apertures through which the stimulating beam was brought to a focus in the very dense layer of sodium vapour formed in the upper part of the tube on heating. For details of the method of observing the laterally emitted light, the original must be consulted.

With white light illumination, the fluorescence spectrum is made up of a large number of hazy lines arranged in bands which lie close together in the vicinity of the *D* lines, widening as the blue region is approached. Coincident with the *D* lines is a hazy band in which two component lines coincident with D_1 and D_2 are recognisable. These lines only appear when the vapour is stimulated with light of the wave-length of the sodium lines, indicating that the electron system which produces these lines is independent of the systems which give rise to the channelled spectra. The region in the immediate neighbourhood of the *D* lines is nearly devoid of light, and the red fluorescence is only readily observed when the density of the vapour is considerable. When approximately monochromatic light is employed as the stimulating source, the emission spectrum consists of a number of more or less regularly spaced bright lines of different intensities. The slightest change in the wave-length of the incident light results in the disappearance of these lines and the appearance of another set. The phenomenon indicates that the sodium atom consists of a number of groups of electrons, the excitation of any one of which sets the entire group in vibration, without, however, disturbing the other groups. Radiations both above and below the exciting radiation are present in the emission spectra, showing that Stokes' law is not obeyed.

H. M. D.

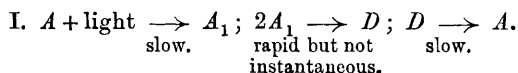
Theory of Photographic Processes. II. Chemical Dynamics of Development, including the Microscopy of the Image. SAMUEL E. SHEPPARD and CHARLES E. K. MEES (*Proc. Roy. Soc.*, 1905, A, 76, 217—234. Compare this vol., ii, 294).—A microscopic study has been made of the influence of exposure and development on the size of grain and number of grains in photographic plates. The general results of the study are in agreement with the theory of development previously proposed. Each grain develops as a more or less isolated system, only uniting to form "aggregates" with other grains at high exposures, when the packing is closer. The thickness of the reaction layer is from 0.02 to 0.04 mm., a value similar to that found by Brunner for many heterogeneous reactions.

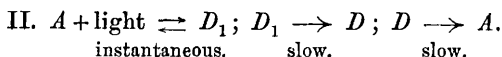
The authors have used extensively the "time of appearance" in studying development kinetics. The velocity of development for most

developers is given by the expression $K = 1/t \cdot \log \gamma_\infty / (\gamma_\infty - \gamma)$, and it is found that the temperature-coefficient of the velocity frequently exceeds the value to be expected from the diffusion theory. Consideration, however, of the various conditions shows that a high temperature-coefficient in development does not necessarily mean that the velocity is that of a chemical reaction. The authors believe that the action of soluble bromides furnishes a means of distinguishing between diffusion velocity and chemical velocity. Consideration of that action and of the reversibility of development makes it probable that the development process generally takes place in two phases. In the first period, the chemical velocity is low compared with that of diffusion, in the second period the contrary holds. It is the velocity of the second period which is usually measured. J. C. P.

Reversible Photochemical Reactions in Homogeneous Systems. Anthracene and Dianthrane. II. ROBERT LUTHER and FRITZ WEIGERT (*Zeit. physikal. Chem.*, 1905, **53**, 385—427. Compare Abstr., 1904, ii, 463).—The earlier investigation has been extended and supplemented. The curve obtained by plotting the concentration of dianthrane at the equilibrium point against the concentration of anthracene in the solution approaches a limit without exhibiting a maximum. The extent of absorption in anthracene (*A*) and dianthrane (*D*) solutions has been studied, and it is found that the absorptive power of dianthrane is small compared with that of anthracene. The velocity of the photochemical reaction $A \rightarrow D$ depends on the same factors as determine the equilibrium point. The velocity of the contrary reaction $D \rightarrow A$ is not affected by light, and the temperature-coefficient in this case is that of an ordinary chemical reaction. A rise of temperature diminishes, *ceteris paribus*, the concentration of dianthrane at the equilibrium point, but has no appreciable effect on the velocity of the reaction $A \rightarrow D$.

The general formula (due to Wittwer and Nernst) for the fundamental law of photokinetics does not represent the experimental results of the authors' work. Consideration of photochemical reactions hitherto studied indicates that these are always of the first order, and this leads to the following formulation of the fundamental law of photokinetics: "The quantity of a substance sensitive to light which undergoes change in the volume dv per unit of time is proportional to the light absorbed during the same time by the substance in the volume dv ." If this is applied to the case under consideration, it may be shown, in harmony with the observed facts, that the concentration of dianthrane at the equilibrium point approaches an upper limit as the concentration of anthracene increases. Quantitative agreement, however, between calculated and observed effects could not be obtained for points short of this upper limit. To secure agreement, the authors suppose that intermediate substances with absorptive power are formed in the reaction. The suggestions made in this direction are indicated below:





A_1 is termed "photoanthracene," and D_1 "photodianthracene." With these hypotheses, it is possible to interpret all the experimental results obtained. J. C. P.

Triboluminescence. C. S. STANFORD WEBSTER (*Chem. News*, 1905, 92, 185).—Large crystals of salicylic acid placed on flannel and crushed against a glass plate or shaken violently in a bottle emit brilliant flashes visible in the dark. The natural acid is less active than the artificial, but both respond to radium to an unusual degree for organic triboluminescent compounds of the first order. A sheet of ground glass mounted in a frame with a handle is found convenient for examining hard substances for triboluminescence, rubbing them on the rough side and observing from the other. D. A. L.

Triboluminescence in the Acridine Series. GILBERT T. MORGAN (*Chem. News*, 1905, 92, 219).— $\beta\beta$ -Dinaphthacridine either in the form of straw-coloured needles or of transparent, amber-coloured prisms, when crushed between ground glass plates emits a vivid, yellow luminescence until pulverisation is complete. The luminescence is also observed when the amber-coloured prisms adhering to the sides of the crystallising vessel are scraped with a spatula. Under similar treatment, triboluminescence is not manifested by the yellow hydrochloride, hydriodide, methiodide, or ethiodide of $\beta\beta$ -dinaphthacridine, or by acridine itself. D. A. L.

Radioactivity of the Boric Acid Suffioni of Tuscany and the Amount of the Emanation contained therein. RAFFAELLO NASINI, FRANCESCO ANDERLINI, and MARIO G. LEVI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 70—76).—The authors have examined the radioactivity of the gases evolved from the boric acid suffioni of Tuscany by the electroscopic method. The dispersion per hour in an Elster and Geitel electroscope with a metal bell, 33 cm. high and 19 cm. in diameter and hence 9300 c.c. in capacity, varies between 500 and 20,000 volts, the lowest value being obtained with gases from the suffioni of Travale, which contain the least amount of boric acid. The radioactivity does not depend on the pressure, temperature, depth, or content of carbon dioxide or water vapour of the gases, and that of any one suffione does not vary with time. The gases of Lardarello, which are among the most radioactive, contain about 1.5×10^{-5} cm. of emanation per cubic metre; after absorption of the carbon dioxide and hydrogen sulphide by potassium hydroxide, the dispersion is raised from 12,000 to 200,000 volts per hour, an increase which is exactly in proportion to the amount of the diminution in volume of the gas. T. H. P.

Radioactive Constituents of the Deposits of Echallon and Salins Moutiers. G. A. BLANC (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 322—328. Compare this vol., ii, 221).—On separating the radio-

active constituents of the deposits from these mineral springs, it is found that the precipitated sulphate increases in radioactivity only very slightly after precipitation, thus differing from other radium preparations; possibly another active element is present with the radium in the insoluble sulphate. The precipitate obtained by means of ammonia is several hundred times more active than thorium hydroxide. The fall in the activity of the emanations and in the induced activity corresponds exactly with that of the thorium salts. The radioactive phenomena observed with thorium salts are due not to an intrinsic property of the element itself, but to the presence of traces of a highly active element, analogous in its chemical characters with thorium and hence difficult to separate from it. T. H. P.

Radioactivity of some Springs in the Southern Viennese Thermal Zone. HEINRICH MACHE and STEFAN MEYER (*Monatsh.*, 1905, 26, 891—897. Compare this vol., ii, 498).—The authors have determined the radioactivity of the water from various springs in Fischau, Vöslau, and Baden, as also from the Theresienbad and from a spring in the Türkenstrasse in Vienna. The results are given in tabular form. The Theresienbad and Türkenstrasse springs are only slightly radioactive; the Baden springs are much more highly radioactive than the Fischau and Vöslau springs. The ratio, *emanation in water : emanation in gas*, is approximately the same, 0.22—0.28, for each spring, and corresponds with the normal equilibrium at the relatively low temperatures of these springs.

The ratio, *emanation in water : emanation in gas*, calculated from Henrich's results for the Adler spring and the Kochbrunnen in Wiesbaden (this vol., ii, 221), 0.017—0.031, shows that that author's determinations are not comparable with each other, or that in these springs the gas, and not the water, is primarily active.

The radioactivity of the emanation from the Fischau springs decays to half of its initial value in 3.82 days, and has $\lambda(\text{sec.}) = 4.76 \times 10^5$; the corresponding values obtained with the emanation from the Vöslau springs are 4.02 days and $\lambda(\text{sec.}) = 5.01 \times 10^5$; and from the Baden springs, 3.86 days and $\lambda(\text{sec.}) = 4.81 \times 10^5$. G. Y.

Radioactive Minerals. ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1905, A, 76, 88—101, 312. Compare Boltwood, *Abstr.*, 1904, ii, 666; 1905, ii, 295).—The amount of radium in a mineral is proportional to the uranium. The investigation of this point demonstrated the existence of uranium in some minerals (for example, monazite) not previously known to contain it. Thorium minerals invariably contain the uranium-radium combination, an observation which possibly indicates that thorium is producing uranium. Helium occurs only in very minute quantity, unless thorium is present, and hence the helium in minerals is probably produced more by thorium than by radium. Thorium minerals vary much in emanating power; some retain nearly all their emanation, others give off large quantities. J. C. P.

A Radioactive Substance discovered in the Transvaal and Experiments connected therewith. R. LEWIS COUSENS (*Chem. News*, 1905, 92, 203—206, 213—215).—An alluvial deposit traced to

the overflow of a volcanic vent exhibited radioactivity, and by washing and panning yielded about 0.2 per cent. of material consisting of inactive silica and radioactive zircon, rutile, magnetite, and ilmenite, with perhaps a very small quantity of other minerals. The activity was greater from the material in a closed than in an open vessel. When dissolved in hydrochloric acid and precipitated successively with ammonia, ammonium chloride, and ammonium carbonate, the radioactive substance was mainly concentrated in the ammonia-ammonium chloride precipitate. The usual experiments were made with it, when the manifestations usual with radium were observed. It is also precipitated from solution with barium sulphate. The radioactivity is therefore attributed to radium, the latter being regarded as derived from titanium.

D. A. L.

Measurement of the Emanations contained in Liquids. HEINRICH WILLY SCHMIDT (*Chem. Centr.*, 1905, ii, 1072; from *Physikal. Zeit.*, 6, 561—566).—The metal flask which contains the liquid to be examined is fitted with two taps, to one of which india-rubber tubing is attached and to the other an india-rubber ball. Both are connected with the vessel in which the emanation is to be measured. The electroscope is placed outside the vessel, and is connected with the substance inside the vessel by means of brass strips with amber insulation. The movement of the aluminium leaf is measured to within about 0.05 volt by means of a microscope. After thoroughly shaking the liquid in the flask for half a minute, the moist air is driven into the measuring vessel by means of the rubber ball. Formulæ for the calculation of the effect of induced activity are given in the original paper and the calculated corrections are arranged in tables. The absorption-coefficients for radium emanations have been determined, and found to be similar to those obtained by R. Hofmann.

E. W. W.

The Ultimate Disintegration Products of the Radioactive Elements. BERTRAM B. BOLTWOOD (*Amer. J. Sci.*, 1905, [iv], 20, 253—267).—To obtain knowledge regarding the ultimate disintegration products of radioactive elements, careful study of the composition of radioactive minerals is necessary. The latter may be classified as primary or secondary according to their geological age as compared with that of the parent rocks in which they occur, that is, where they appear to be of a later date they are regarded as secondary. In all analyses of uranium minerals, especially primary minerals, lead is always present, and hence is indicated as a final product, it being further noteworthy that the atomic weight of lead is almost identical with that of radium-G, if each radium change is accompanied by the evolution of an atom of helium. Thorium is also usually associated with uranium, and it has been suggested that possibly thorium is the parent substance of uranium; as, however, uranium minerals containing much thorium also contain much helium, the author considers it more probable that thorium is a disintegration product of uranium. Bismuth and barium are also indicated as final products and also probably actinium. It is remarkable that many radioactive minerals appear to

be hydrated, and many contain hydrogen (Ramsay, Collie, and Travers, *Trans.*, 1895, **67**, 686) when the conditions are such that penetration of water from without appears impossible, and hydrogen must therefore be regarded as a possible final product, whilst similar evidence suggests argon. The analyses of a number of samples of uraninite are given, and it is noteworthy that the highest proportions of lead and helium with respect to uranium are found in those primary minerals which occur in the oldest geological formations; and, further, that those containing the greatest proportion of thorium are generally the most hydrated. The author suggests the above as hypotheses deserving investigation rather than as definite conclusions.

L. M. J.

Atomic Weight of Radium and the Periodic System.

HARRY C. JONES (*Amer. Chem. J.*, 1905, **34**, 467—471).—Evidence based on the periodic system is brought forward to demonstrate that the atomic weight of radium approaches 258, the value given by Runge and Precht (*Abstr.*, 1903, ii, 346), rather than 225, the value found by Madame Curie.

E. G.

A New Element, Radiothorium, the Emanation of which is identical with that of Thorium. Sir WILLIAM RAMSAY (*J. Chim. phys.*, 1905, iii, 617—624).—A Ceylonese mineral, which has been named thorianite (*Abstr.*, 1904, ii, 744, 745), was found to yield, on heating to redness, about 9 c.c. of helium per gram, that is, nearly four times as much as that obtained from cleveite. It also contained radium and thorium, but during their separation a new element was discovered, which differs from radium by forming a soluble sulphate and from thorium in forming an insoluble oxalate which is not soluble in excess of ammonium oxalate. This element was found to form radioactive salts, which give off an emanation identical with that of thorium. The identity is seen by the rate of decay and by equal period of induced activity. The oxide after heating is self-luminous and very rich in β -rays. The emanation is lighter than air, for the effect on a screen is more marked when the latter is above the salt than when it is below. The same obtains for the emanations of actinium and emanium, but the emanations are not the same. The radioactivity is very great, the emanation produced from a few mg. being equal to that given by 500,000 times the mass of thorium. The author hence considers it very probable that the radioactive power of thorium is to be attributed to small quantities of this element, radiothorium, and suggests the following series: (1) inactive thorium, (2) radiothorium, (3) thorium X, (4) emanation, (5) thorium A, (6) thorium B, (7) (?), (8) helium (see also following abstract).

L. M. J.

A New Radioactive Element which gives rise to the Thorium Emanation. OSKAR HAHN (*Ber.*, 1905, **38**, 3371—3375).—A continuation of experiments described previously (*Abstr.*, 1905, ii, 432; compare also preceding abstract). Details are given of the isolation of 10.9 mg. of an intensely active substance, *radiothorium*, which produces 700,000 times as much thorium emanation

per unit of time as is produced by thorium itself. Radiothorium is certainly not identical with thorium X, because it has a nearly constant radioactivity; it is also apparently chemically distinct from thorium itself. But its emanation is identical with the thorium emanation, λ having the value $1.3 \cdot 10^{-2}$, and the half value being reached after 53.3 seconds; the emanation is apparently a gas less dense than air, as it rises when produced. Radiothorium behaves like thorium in ceasing temporarily to give off its emanation when heated. It appears probable that radiothorium is the active constituent of ordinary thorium, being related to the latter in the same way as radium is related to uranium.

W. A. D.

Thorium X and the Induced Thorioactivity. F. VON LERCH (*Monatsh.*, 1905, 26, 899—929).—The induced thorioactivity, but not thorium X, is precipitated from the hydrochloric acid solution of thorium X by magnesium, iron, zinc, amalgamated zinc, nickel, lead, copper, or aluminium. The induced thorioactivity, sometimes along with traces of thorium X, is precipitated on electrolysis of acid thorium X solutions; but thorium X is precipitated along with metals from alkaline solutions. Precipitates, the activity of which diminishes to half of the initial value in more than 1 and less than 10.6 hours, contain thorium B and thorium A, the activities of which decay to half-value in 1 and 10.6 hours respectively. The amount of thorium B in a solution of induced thorioactivity is proportional to the amount of thorium A; whilst in a thorium X solution the amounts of thorium A and thorium B present are proportional to thorium X.

G. Y.

Deflection of α -Rays from Radium and Polonium. A. STANLEY MACKENZIE (*Phil. Mag.*, 1905, [vi], 10, 538—548. Compare Rutherford, *Abstr.*, 1903, ii, 256).—The deviations of a beam of α -rays in a magnetic and an electrostatic field have been measured. The beam of rays, after passing through two slits at one end of an exhausted vessel, traversed the field of force and was received at the opposite end on a glass plate coated on the inside with a thin layer of powdered zinc sulphide. The position of the incident beam was determined by placing a photographic plate in close contact with the outer side of this screen.

On account of the heterogeneous character of the α -rays from radium, considerable dispersion takes place in a magnetic field.

If m , e , and v denote respectively the mass, charge, and velocity of the α -particles, the mean value obtained for mv/e for the middle line of the spectrum is 3.0×10^5 C.G.S. electromagnetic units.

The observed electrostatic dispersion was considerably smaller than the electromagnetic, and the mean value of mv^2/e for the middle rays is 4.11×10^{14} . From these numbers, v (for the mean ray) = 1.37×10^9 cm. per second, and $m/e = 4.6 \times 10^3$ electromagnetic units. Allowing for the absorption by the mica plate separating the radium preparation from the slit tube, the velocities of the slowest, average, and fastest rays are 1.18, 1.45, and 1.74×10^9 cm. per second. Assuming that the charge on the α -particle is the same as that carried by the hydrogen atom, it follows that the mass of the former is 2.2 times

that of the latter and this suggests that the α -particle is a hydrogen molecule.

From measurements of the deflexion of the α -rays from polonium which exhibit no appreciable dispersion, the value of $mv/e = 3.30 \times 10^5$. Assuming m/e is the same as for the radium α -particles, it follows that the velocity of the particles from polonium is greater than that of the average α -particles from radium.

H. M. D.

α -Particles of Radium. W. H. BRAGG (*Phil. Mag.*, 1905, [vi], 10, 600—602. Compare Bragg and Kleeman, this vol., ii, 5; Rutherford, *ibid.*, 495).—The view expressed in a previous paper, that the whole of the energy of the α -particles is spent before they cease to ionise, is corrected. Rutherford's experiments on radium-C indicate that only a portion of the energy is used up before this condition is reached. The particles, however, lose the power of ionisation at exactly the same speed in all gases. This is the only possible conclusion to be drawn from experiments on mixtures of gases. The data obtained in experiments on the amount of ionisation at different distances from the source of the α -particles indicate that the ionisation varies inversely as the square of the velocity of the particles.

H. M. D.

Emission of Negative Corpuscles by the Alkali Metals. JOSEPH J. THOMSON (*Phil. Mag.*, 1905, [vi], 10, 584—590).—It has been found that the alkali metals emit negative corpuscles even when all external light is excluded. An evacuated vessel containing rubidium or an alloy of sodium and potassium and a well-insulated gold-leaf electroscope is enclosed in a light-tight box. The divergence of the leaves is measured by means of a reading microscope, passing through the side of the box, the leaves being momentarily illuminated by a faint light transmitted through a red glass window. During the intervals of illumination, the leak of the instrument is much greater than in the dark, but this part of the leak can easily be separated from the slower leakage taking place in the dark. When the gold leaves are charged with negative instead of positive electricity, there is no perceptible leak and the positive leak is also stopped by a transverse magnetic field. Traces of hydrogen produce a very large temporary increase in the rate of leakage; the emission of corpuscles is therefore greatly increased during the absorption of hydrogen by the alkali metals. No evidence of the emission of corpuscles is obtained from lead, silver, or mercury. When sodium is converted into vapour in an exhausted vessel containing two glass tubes down which run wires having a difference of potential of 600 volts, deposition of the sodium takes place almost entirely on the tube containing the negative wire, indicating that the sodium atoms are positively charged. The author supposes that most substances emit corpuscles under certain conditions and that the energy of these is derived from the atoms of the corpuscle-emitting substances. In the interior of a substance, the energy of the corpuscles is ultimately transformed into heat energy, and this should cause the interior of a mass of a substance to be hotter than the surface, the difference of temperature depending

on the amount of energy transformed, the size of the body, and its thermal conductivity. For a body of the size of the earth having a conductivity equal to 0.01, the value of this difference would be 3000° if the amount of atomic energy thus transformed into heat per cubic centimetre in 100 million years is approximately equal to the heat required to raise the temperature of 1 gram of water by 1.5° .

H. M. D.

Method of Transmission of the Excited Activity of Radium to the Cathode. WALTER MAKOWER (*Phil. Mag.*, 1905, [vi], 10, 526—532. Compare Rutherford, 1900, ii, 352).—The dependence of the amount of excited activity deposited in a given time on a negatively-charged rod exposed to a constant quantity of emanation on the pressure of the surrounding gas has been investigated. The deposited activity is independent of the difference of potential between the electrodes over a considerable range. At low pressures, the activity acquired diminishes as the pressure is decreased and varies with the distance between the electrodes. As this distance increases, the values of the pressure at which a diminution in the amount of deposited activity is observable become smaller. The experiments indicate that, at low pressures, the excited activity produced from radium emanation contained in a closed vessel is not confined to the cathode, but is distributed over the walls of the vessel and appears both on the anode and cathode even in a strong electric field. It is supposed that the excited activity at the moment of its production is unchanged, and that the collision of the particles with gas molecules results, in a certain percentage of cases, in the expulsion of electrons, leaving the excited activity positively charged. In accordance with this hypothesis, it is found that the activity deposited by a given quantity of emanation in a given time is not increased when the number of ions present in the containing vessel is increased by external means.

H. M. D.

Method of Transmission of the Excited Activity of Radium to the Cathode. W. H. JACKSON (*Phil. Mag.*, 1905, [vi], 10, 532—537).—It is shown that the deviations of the experimental results contained in the preceding paper from those required by the theory that the molecules of excited activity are initially uncharged, but become so in consequence of the collision with gas molecules, are actually less than the errors of observation.

H. M. D.

Electrification produced by Radium Rays. AUGUSTO RIGHI (*Nuovo Cim.*, 1905, [v], 10, 13—17).—The method of working adopted by the author consisted in charging a disc of the substance under examination at a feeble positive potential, for example, +0.4 volt, subjecting it to the action of β -rays from 0.015 gram radium bromide, and measuring the time required for the disc to assume a potential of -0.4 volt. The general result arrived at is that the variation of potential per unit of time decreases as the atomic weight of the element of which the disc is made increases. When the substance is in the form of very thin leaves, the charge acquired by it is virtually zero. Hence such thin leaves can be employed for pre-

paring a conducting coating for measuring the charges acquired by dielectrics on which radium rays impinge.
T. H. P.

Diminution of Resistance produced in Bad Conductors by Radium Rays. AUGUSTO RIGHI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 207—214).—Under the influence of the β -rays from radium bromide, the resistance of light petroleum, oil of turpentine, carbon disulphide, benzene, or olive oil is considerably diminished; with light petroleum, the resistance is only one-sixth of its normal value. The effects obtained with solid dielectrics were small and uncertain. The apparatus used by the author is described.
T. H. P.

Increase of the Conductivity of Water by Radium Emanations. UGO GRASSI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 281—284).—The water employed by the author was mixed with sulphuric acid and potassium permanganate and distilled through a tin condenser into a Jena glass vessel fitted with smooth platinum electrodes, by means of which the conductivity measurements were made. Hydrogen, charged with emanations from 0.002 gram of radium bromide, was passed through the water. In this way, the conductivity was lowered in three days to about one-third of its initial value—from $3.4\text{--}3.5 \times 10^{-7}$ to about 1×10^{-7} reciprocal ohms at about 23° ; the latter value remained unchanged on further passage of the charged hydrogen. After the current of hydrogen was stopped, the conductivity of the water increased rapidly, but the amount of the increase was not constant and seemed to depend on the time during which the hydrogen remained in contact with the radium before being passed into the water.
T. H. P.

Measurement of Potentials in Iodine Vapour. W. MATTHIES (*Sitzungsber. phys. med. Soc. Erlangen*, 1905, 37; reprint).—When a discharge passes through iodine vapour at low pressures in a Geissler tube, a beautiful orange-yellow luminescence is observed at the cathode. This light gives a continuous spectrum extending from red to green. The normal fall of potential at a platinum cathode in iodine vapour is 377 volts; this value is independent of pressure and of current strength. The fall of potential at the anode varies with the pressure and the current strength; the lowest value observed was 66.6 volts.
J. C. P.

Elimination of the Diffusion Potential between Two Dilute Aqueous Solutions by the Insertion of a Concentrated Solution of Potassium Chloride. NIELS BJERRUM (*Zeit. physikal. Chem.*, 1905, 53, 428—440).—The author's experiments show that the use of a concentrated potassium chloride solution for the purpose stated in the title gives very satisfactory results. A formula is deduced for the diffusion potential between a concentrated potassium chloride solution and a dilute solution of a strongly dissociated binary electrolyte.
J. C. P.

Electrical Conductivity of Selenium. MAURICE COSTE (*Compt. rend.*, 1905, 141, 715—717).—The usual method of converting the non-conducting vitreous form of selenium into the conducting metallic variety by fusing the vitreous form between two metallic plates and allowing it to cool slowly (compare Marc, *Abstr.*, 1903, ii, 105) is not satisfactory, since selenium combines with most of the metals, including gold, to form selenides; if, however, the metal plates are replaced by pure carbon, the complications due to the presence of the selenides are obviated. The conversion of vitreous silicon into the metallic variety is accompanied by a change in structure, the substance becoming more porous and not exhibiting a constant electrical resistance until after the lapse of some hours; thus, the resistance of a rod of selenium having the dimensions 90 mm. \times 1 mm. \times 0.5 mm. was 44,000 ohms immediately after conversion, 60,000 ohms after one hour, 63,500 ohms after two hours, 78,000 after twenty-four hours, and constant at 86,000 ohms after forty-eight hours. M. A. W.

Temperature-coefficients of Conductivity in Aqueous Solutions and the Effect of Temperature on Dissociation. HARRY C. JONES and AUGUSTUS P. WEST (*Amer. Chem. J.*, 1905, 34, 357—422).—A *résumé* is given of previous work on this subject.

A study has been made of the effect of temperature on dissociation between 0° and 35°; the temperature-coefficients of conductivity, expressed in percentage of conductivity units, have been calculated by means of the Kohlrausch formula, and the influence of temperature on these coefficients has been investigated.

The conductivity of aqueous solutions of the following substances at various concentrations and at temperatures between 0° and 35° has been determined. Ammonium chloride and bromide; sodium bromide, iodide, carbonate, and acetate; potassium chloride, bromide, iodide, nitrate, sulphate, carbonate, and ferrocyanide; potassium hydrogen sulphate; calcium chloride and bromide; strontium bromide; barium chloride; magnesium chloride; zinc sulphate; manganese chloride and nitrate; cobalt chloride and nitrate; nickel chloride and nitrate; copper chloride and nitrate; hydrochloric, nitric, sulphuric, and oxalic acids.

The results are given in tabular form, and include the molecular conductivities, comparison of these values with those obtained by other observers, the temperature-coefficients in conductivity units, the temperature-coefficients per cent., and the percentage dissociation. It is found that in all cases there is a large increase in conductivity due to increased ionic mobility, and that the percentage dissociation and the percentage temperature-coefficients of conductivity decrease as the temperature rises from 0° to 35°. The effect of temperature on the temperature-coefficients of conductivity, expressed in conductivity units, is different in the case of salts from that in the case of acids; with salts, they increase with rise of temperature, whilst with acids they decrease.

These results are shown to be in harmony with the observation of Ramsay and Shields (*Trans.*, 1893, 63, 1089), that the association of water becomes less as the temperature is raised, and with the hypo-

thesis of Dutoit and Aston (Abstr., 1897, ii, 546), which states that as the association of a solvent decreases, its dissociating power is diminished. The fact that the dissociation decreases with rise of temperature is also in agreement with the conclusions to be drawn from the results of Vonwiller (*Phil. Mag.*, 1904, [vi], 7, 655), showing a decrease in the dielectric constant of water with rise of temperature, and the Thompson-Nernst hypothesis connecting the dissociating power of a solvent with its dielectric constant. The temperature-coefficients of conductivity, expressed in percentage of conductivity units, decrease with rise of temperature, and this fact is in accordance with the maximum in the conductivity-temperature curve of an electrolyte as pointed out by Bousfield and Lowry (Abstr., 1903, ii, 52).

E. G.

Electrolytic Dissolution of Platinum. RUDOLF RUER (*Zeit. Elektrochem.*, 1905, 11, 661—681).—A platinum anode immersed in a solution of sulphurous acid or ferrous sulphate in 50 or 66 per cent. sulphuric acid is dissolved slowly by an intermittent current. The current must be strong enough and must pass for a sufficient length of time to impart a suitable anodic potential to the platinum; the interruption must be long enough to permit the reducing agents to diminish this potential below a certain point. Under similar conditions, a platinum cathode is dissolved in presence of a strong oxidising agent such as persulphuric or chromic acid. Alternate cathodic and anodic polarisation gives the same result. Measurements of the polarisation show that the anodic potential of at least -1.20 volts (compared with a hydrogen electrode in sulphuric acid of the same strength) is required to give any dissolution of the platinum and that the dissolution increases as the potential increases; the alternate cathodic potential of -0.7 volt gives the maximum dissolution. If the cathodic polarisation is pushed so far that the potential 0 is reached and hydrogen begins to be evolved, no platinum is dissolved.

A very careful repetition of the experiments of Brochet and Petit (this vol., ii, 673) showed that no dissolution whatever occurs with the current from an aluminium rectifier.

The whole of the results are readily explained by assuming the formation of a layer of platinum peroxide (Abstr., 1903, ii, 407). From the quantity of platinum dissolved by alternate anodic and cathodic polarisation, it is shown that the thickness of the layer of oxide is at least 0.09×10^{-6} mm., which is less than the diameter of a molecule.

T. E.

Electromotive Behaviour of Dilute Amalgams. J. F. SPENCER (*Zeit. Elektrochem.*, 1905, 11, 681—684).—Amalgams of zinc, cadmium, lead, thallium, and copper are prepared by electrolysis, and measurements of the *E.M.F.* between the amalgam and the pure metal in a normal solution of a metallic salt are made. The differences between the potentials of the amalgams can be calculated fairly well by means of Nernst's formula, assuming the molecule of the metal dissolved in the mercury to contain two atoms, except in the case of thallium, which is monatomic. Some of the amalgams of zinc and copper are less noble than the pure metals.

T. E.

Electromotive Behaviour of Molybdenum and its Analogies with that of Chromium. LUIGI MARINO (*Gazzetta*, 1905, 35, ii, 193—224).—Although molybdenum, like chromium, is capable of functioning as a bi-, ter-, or sexa-valent element, electrochemically it exists only in one degree of combination—the sexavalent. Molybdenum can, under widely varying conditions, occur in two different states, namely, active and passive. With these two states correspond two definite values of the *E.M.F.*, and between these values lie an indefinite number of others answering to the infinite number of conditions of the surface of the metal; the same has been shown by Hittorf to hold for chromium.

The metal is active when in contact with strongly oxidising solutions, such as those of chlorine, bromine, nitric acid, or chloric acid, at the ordinary temperature; further, it is active in solutions of highly oxygenated salts, but only at temperatures rising with the dilution, and also in concentrated solutions of certain other acids only capable of dissolving it at their boiling points, the *E.M.F.* being here identical with that exhibited in solutions able to dissolve it readily.

The inactive condition of the metal is only possible for certain values of the current density, a fact which indicates the great influence of the latter magnitude on the surface of the metal. This influence is shown most distinctly in solutions of substances rich in oxygen, such as nitric acid and nitrates.

Neglecting the slight influences exerted by different electrolytes, the highest value of the *E.M.F.* after the metal has acted for some seconds as a cathode is 1.50 volts for the active condition and 0.20 volt for the passive condition. The inactive state of the metal is unstable and, as soon as its cause is removed, reverts to the active condition, the change proceeding more rapidly than with chromium.

The behaviour of molybdenum lends support to Hittorf's idea, that a class of substances may exist the chemical energy of which is not transformable into electrical energy.

T. H. P.

Cathode Potentials necessary for the Electrolytic Deposition of Certain Metals from Solutions of their Sulphates. GIULIO COFFETTI and FRITZ FOERSTER (*Ber.*, 1905, 38, 2934—2944. Compare Küster, *Abstr.*, 1901, ii, 555).—The authors have determined the cathode potentials necessary for the electrolytic deposition of copper, cadmium, zinc, cobalt, nickel, and iron from normal solutions of their sulphates, using different current densities, a platinum cathode, and an anode of the metal in question, at 20°. The *E.M.F.* was measured against an *N/10* calomel electrode, the potential of which, $\epsilon_h = -0.336$ volt. As cadmium is deposited irregularly from the solution of its sulphate, 10 per cent. of hydrofluosilicic acid was added to the electrolyte.

Hydrogen is evolved on electrolysis of very slightly acid solutions of iron, nickel, and cobalt sulphates; in these cases, the amount of metal deposited is given as a percentage of the current employed.

The variation of the cathode potential with the current density is shown by a series of tables and curves. The potentials necessary

form an ascending series, copper, cadmium, cobalt, nickel, iron, and zinc.

The results for nickel and iron agree with the values given by Muthman and Fraunberger for the difference of potential of these metals (*Sitzungsber., Bayer, Akad. Wiss.*, 1904, 34, 201). G. Y.

Rate of Recombination and the Size of Gaseous Ions. JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1905, 13, 170—173).—

If two oppositely charged ions start from rest, their attraction will cause them to form one system, and they will cease to act as ions. If, however, the kinetic energy T of the ions is greater than e^2/r , where e is charge on the ions and r their distance, they will again separate, and hence for recombination the ions must approach to a distance $r < e^2/T$, and as T is dependent solely on temperature, this limiting distance is the same for all ions, and the value is calculated as 1.4×10^{-6} cm. From this value and that of the average distance between ions, the author calculates the value for the number of recombinations per second as $n\pi r^2 V$ (where n is the number of ions) per unit volume. This equated to an^2 , where a is the coefficient of recombination, leads to $a = 1.5 \times 10^{-6}$ if the ions have the same mass as the molecules. This value, although of the same order, is slightly higher than the value obtained otherwise, so that the mass of the ion is somewhat greater than that of the molecule. In strong electric fields, it is clear that a will decrease considerably. The attraction of ions for uncharged molecules is next considered, and it is shown that in general the charged molecule will recombine and form a complex ion, but that this process of aggregation will be limited, and will stop at an earlier stage at high temperatures than at low ones. L. M. J.

Faraday's Law in Reference to the Glow Discharge in Gases. CLARENCE A. SKINNER (*Chem. Centr.*, 1905, ii, 1215; from *Physikal. Zeit.*, 6, 610—614).—In the apparatus used for the experiments on the glow discharge in gases, the anode was made of the sodium-potassium alloy NaK; the cathodes of various metals were used, and could be changed without being exposed to the atmosphere. When the tube was filled with helium, the pressure, measured by a Macleod manometer, was found to increase regularly owing to the liberation of hydrogen from the cathode. The quantity of hydrogen formed was at first in accordance with Faraday's law, but decreased after a time. Aluminium, bismuth, cadmium, copper, gold, lead, magnesium, nickel, platinum, silver, steel, tin, and zinc were found to behave in practically the same way. When the tube was filled with mercury which had been distilled in a vacuum and had not been exposed to the air, no hydrogen was evolved. Since, when the tube contained hydrogen, the pressure remained constant, the anode must have absorbed the gas as rapidly as it was evolved, but after saturation of the anode the pressure began to rise slowly. Zinc which had been distilled in a vacuum and exposed to air did not cause any decrease in the quantity of gas liberated; hydrogen was first formed and then nitrogen, and if air was allowed to enter the tube the evolution of gas again increased. When carbon electrodes were used and the tubes were freshly filled with helium, nitrogen was con-

tinuously liberated, together with a small quantity of hydrogen, and the quantities were approximately in accordance with Faraday's law. By allowing the apparatus to remain at rest, the electrodes recovered their former condition by a process of diffusion from the interior to the surface. When the tube was filled with nitrogen, the absorption of the gas by a carbon electrode was found to follow Faraday's law. In the phenomenon of glow discharge in gases, therefore, the current is carried from the commencement by means of the atoms of the gases.

E. W. W.

Mercury Arc Lamp in Vessels of Fused Silica. ERNST HAAGN (*Chem. Centr.*, 1905, ii, 803; from *J. Gasbel.*, 48, 613—614).—The properties of fused silica render it more suitable for the construction of mercury lamps than ordinary glass. The intense light emitted by the lamp has an unpleasant colour, and affects the skin like a frost-bite; it is rich in ultra-violet rays, which are transmitted more perfectly by silica than by glass. The spectrum consists of a few lines, and the red portion is totally absent. The oxygen of the air surrounding the lamp becomes ozonised. The use of amalgams offers no advantage. The light depends on the vaporisation of the metals, the lamp becoming filled with the vapour of those metals which have the lowest vapour tensions, whilst the less volatile remain at the electrodes. The arc behaves like a free conductor carrying a current, and is affected by a magnet, placing itself in a position which is perpendicular to the lines of force. Hall's phenomenon may be demonstrated more readily by means of the lamp than by any other method. If the lamp is cooled by water, the light becomes considerably richer in ultra-violet rays.

E. W. W.

New Type of Electric Furnace, with a Redetermination of the Melting Point of Platinum. JOHN A. HARKER (*Proc. Roy. Soc.*, 1905, A, 76, 235—250).—The essential part of the furnace is a tube of solid electrolytically conducting material, such as is used in the Nernst lamp. This tube, which is connected through a regulating resistance with the terminals of a 100—500 volt circuit, is placed centrally in a longer tube of hard porcelain or fire-clay, the space between the tubes being packed with pure zirconia powder. The outer tube is wound round with nickel wire, which is connected with an appropriate source of current, and acts therefore as a heating jacket. It was found that the control of the temperature in the inner tube between 800° and 2000° was so good that well-defined melting points could be obtained with very small quantities of substance. Thus, with a thermo-junction of bare platinum and platinum-rhodium or platinum-iridium, very concordant values were obtained for the melting point of the platinum which formed the junction. Many determinations were made, and the melting point of platinum is found to be $1710^{\circ} \pm 5^{\circ}$, a value considerably lower than the numbers previously found (for example, 1780°; see Holborn and Wien, *Abstr.*, 1896, ii, 87). The extrapolation to such a high temperature of the formula for the *E.M.F.* is justified by the fact that a good value is obtained similarly for the melting point of nickel.

J. C. P.

Magnetic Qualities of Some Alloys not containing Iron.

JOHN A. FLEMING and R. A. HADFIELD (*Proc. Roy. Soc.*, 1905, A, 76, 271—283).—An exact study of the magnetic properties of two alloys containing copper, aluminium, and manganese has been made. The first alloy contained Mn, 22.42 per cent.; Cu, 60.49 per cent.; Al, 11.65 per cent.; C, 1.5 per cent.; Si, 0.37 per cent.; Fe, 0.21 per cent.; intermingled slag (mostly MnO and SiO₂), 2—3 per cent. The approximate composition of the second alloy was Mn, 18 per cent.; Cu, 68 per cent.; Al, 10 per cent.; Pb, 4 per cent. These alloys have poor mechanical properties, are brittle, and cannot be forged.

The first alloy exhibits magnetic properties analogous to those of a feebly ferromagnetic material. It exhibits the phenomena of magnetic hysteresis and of magnetic retentivity and coercivity. It is not merely magnetic, but can be permanently magnetised. The magnetic qualities of the second alloy are generally similar to those of the first alloy. These results lead the authors to conclude that the magnetic properties of these alloys must be based on a similarity of molecular structure with the familiar ferromagnetic metals. These metals are probably composed of molecular groups which are permanently magnetic; the process of producing or changing the evident magnetisation of a mass of these metals would then consist in arranging or disturbing the positions of these molecular magnets. The alloys examined by the authors are instances of fairly strong ferromagnetism produced by mixing non-magnetic metals, and hence it follows that ferromagnetism *per se* is not a property of the chemical atom, but of certain molecular groupings. If this is so, it may be possible to prepare alloys which are more strongly magnetic than iron itself.

J. C. P.

The Thermo-electric Junction as a means of determining the Lowest Temperatures. Sir JAMES DEWAR (*Proc. Roy. Soc.*, 1905, A, 76, 316—325).—A German silver-platinum thermocouple is found to be trustworthy as a thermometric agent at the lowest steady temperature that could be obtained. According to the indications of this instrument, the melting point of hydrogen is 15.7° absolute, and a temperature of 14.4° absolute can be reached by exhausting solid hydrogen. These are both mean values.

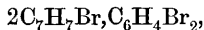
J. C. P.

Relation of the Specific Heats of Crystalline Substances to Temperature. ALEX. D. BOGOJAWLENSKI (*Chem. Centr.*, 1905, ii, 945—947; from *Skriften Dorpater Naturfor. Ges.*, 1904, 13, 1—73).—The specific heats of ten organic compounds which had been purified by crystallisation from different solvents, by fractional distillation, or by distillation in steam, have been determined at different temperatures by means of a mercury calorimeter. The specific heats of these compounds, with the exception of *p*-dibromobenzene and to some extent naphthalene, were found to increase considerably with rise of temperature. This abnormal behaviour is doubtless due to the presence of impurities, which cause the softening and partial liquefaction of these substances which was observed to take place at tempera-

tures below their melting points. This hypothesis was confirmed by the results obtained when the specific heats were determined by a "reversed" method in which the substance at the ordinary temperature was introduced into a heated calorimeter. For absolutely pure substances such a method should give higher values than the direct method, and this was found to be the case for *p*-dibromobenzene, naphthalene, quartz, topaz, and iron, but lower values were obtained for the other organic compounds. Tables showing the specific heats of *p*-dibromobenzene, *m*-chloronitrobenzene, benzil, α -crotonic acid, phenylacetic acid, diphenylamine, *o*-nitrophenol, and naphthalene at temperatures above 0° , and of benzene, naphthalene, and ice at temperatures below 0° , are given in the abstract. The specific heat of pure compounds varies only slightly with temperature, and the function $c=f(t)$ appears to be a linear one.

Experiments have also been made to determine the specific heats and temperatures of solidification of mixtures of *p*-dibromobenzene and naphthalene, sulphonal and benzil, and *p*-dibromobenzene and *p*-bromotoluene. The first mixture gives the simplest curves and showed eutectic points at 47.6° and 80.4° . The specific heats of the mixture not only increase rapidly with rise of temperature at temperatures considerably below that of solidification, but also show a sudden increase at a constant temperature. At this temperature, which is below the eutectic point, the specific heats of all the mixtures change suddenly. The remarkable constancy of the temperature is due to the actual presence of the eutectic mixture, the sudden rise of the specific heat on further heating being caused by the melting of the mixture. The Regnault-Neumann rule for the specific heat of mixtures of crystalline substances holds for the mixtures quoted up to temperatures near the eutectic point, and at temperatures above this the specific heats may be represented by a formula into which the heat of liquefaction enters.

The diagram which represents the relationship of temperatures of solidification to composition in the case of the mixture of *p*-dibromobenzene and *p*-bromotoluene is given in the abstract. The temperatures of solidification of all the mixtures lie above the melting point of *p*-bromotoluene (26.50°) and below that of *p*-dibromobenzene (87.05°), and these compounds therefore form solid solutions although they are not isomorphous; *p*-bromotoluene crystallises in rhombic and *p*-dibromobenzene in monoclinic crystals. The curves intersect at 36.6° , which is the transformation temperature corresponding with the change of the monoclinic into the rhombic crystals. The diagram is divided by the ordinates of this point into two portions, of which one embraces isomorphous mixtures of *p*-bromotoluene with the compound



and the other mixtures of *p*-dibromobenzene with the compound $2C_7H_7Br, C_6H_4Br_2$. The eutectic temperature of the latter mixtures appears to be 36.6° , and the specific heat of these mixtures increases suddenly at about 30° .

From the results of the experiments described above and the consideration of Spring and Kapp's work on lead-tin alloys, it is shown that the relationships of physical condition to temperature and com-

position may be deduced from calorimetric as well as from thermometric data. From the character and position of the points of change of direction of the curves of specific heats of binary mixtures, eutectic mixtures may be distinguished from mixtures of isomorphous and isodimorphous substances.

E. W. W.

Studies with the Liquid Hydrogen and Air Calorimeters.

I. Specific Heats. II. Latent Heats. Sir JAMES DEWAR (*Proc. Roy. Soc.*, 1905, *A*, **76**, 325—340).—With the aid of the calorimeter previously described, the author has determined the specific heats at low temperatures for a large number of substances. Diamond, graphite, and ice are dealt with in greater detail, and the specific heats for these substances are given in the following table :

	+18° to -78°.	-78° to -188°.	-188° to -252·5°.
Diamond	0·0794°	0·0190°	0·0043°
Graphite	0·1341	0·0599	0·0133
Ice	—	0·285	0·146

Further, the specific heat of ice for the range -18° to -78° is 0·463.

The latent heats of vaporisation of oxygen, nitrogen, hydrogen, and air at their respective boiling points have been determined by measuring the gas produced on introducing a known weight of lead into the liquid. The mean values obtained for oxygen, nitrogen, and hydrogen are 51·15, 50·4, and 123·1 calories respectively. The latent heat of vaporisation of air requires further investigation.

J. C. P.

Latent Heat of Vaporisation of Carvacrol and Anethole.

VLADIMIR F. LUGININ (*J. Chim. phys.*, 1905, *iii*, 640—647).—The values for the specific heat and latent heat of vaporisation of carvacrol are found to be 0·5770 and 68·08 cal. respectively. The boiling point being $237\cdot97^{\circ}$, the value for the latent heat leads to a Trouton constant of about 20 and hence indicates the absence of polymerisation. The corresponding values in the case of anethole are 0·5113, $71\cdot5$ cal., $235\cdot2^{\circ}$, and $20\cdot8$, so that in this case also there is no polymerisation.

L. M. J.

Relative Value of Calorimetric Methods. JULIUS THOMSEN (*Zeit. physikal. Chem.*, 1905, **53**, 314—316. Compare this vol., *ii*, 435, 571).—Polemical in reply to Berthelot (this vol., *ii*, 504).

J. C. P.

[**Thermochemical Studies.**] JULIUS THOMSEN (*J. pr. Chem.*, 1905, [*ii*], **72**, 341—342. Compare this vol., *ii*, 231, 435, 571; Lagerlöf, *Abstr.*, 1904, *ii*, 382, 605; this vol., *ii*, 76).—Polemical. A detailed reply to Lagerlöf's objections to his criticisms (this vol., *ii*, 677).

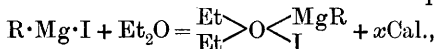
G. Y.

Heats of Mixture of Acids. EMIL BOSE (*Chem. Centr.*, 1905, *ii*, 947—948; from *Physikal. Zeit.*, **6**, 548—553).—The curves which represent the relationship between the heats of mixture and the percentage composition of binary mixtures generally show a distinct change of curvature. If the percentage of water or other independent variable is taken as ordinate, the first portions of the curves are almost

hyperbolic. The data for dilute solutions, however, do not show this relationship (compare von Steinwehr, Abstr., 1901, ii, 641). Thomsen's data may be represented by an equation: $y = ax + bx^2 + cx^3$, in which y is a function of the percentage of one of the components of the mixture. This equation holds with fair accuracy in the case of hydrochloric, hydrobromic, hydriodic, formic, acetic, phosphoric, nitric, and sulphuric acids; the halogen acids and the organic acids seldom show a difference of more than 1 per cent. Whilst the formula gives better results for dilute solutions of nitric acid than Thomsen's formula, it offers no advantage in the case of sulphuric acid. Formulae for the molecular heat of mixture and molecular heat of dilution are also given in the original paper, and the peculiar character of the curves which represent the relationships of heat-tone to percentage of water for solutions of acetic acid and formic acid is also referred to. E. W. W.

Conversion of Organo-magnesium Compounds into Grignard-Baeyer Oxonium Compounds and the Thermochemical Investigation of this Reaction. WLADIMIR TSCHELINZEFF (*Ber.*, 1905, 38, 3664—3673).—The organo-magnesium compounds were prepared in benzene or light petroleum solutions by the addition of about five drops of dimethylaniline (to act as a catalyst; see this vol., i, 40), and were afterwards mixed with dry ether in a calorimeter.

The values obtained for x in the thermochemical equation,



are as follows:

R.	C ₂ H ₅ .	nC ₃ H ₇ .	isoC ₄ H ₉ .	isoC ₅ H ₁₁ .	
x	+12·7	+12·6	+13·3	+12·5	In benzene
x	—	+12·2	—	+12·0	In light petroleum

The same values for x have been obtained by using the solid organo-magnesium compounds as by using light petroleum solutions.

J. J. S.

Specific Heats and Latent Heats of Fusion of Potassium and Sodium. ARCIERO BERNINI (*Nuovo Cim.*, 1905, [v], 10, 5—13).—The author's measurements show that: (1) the specific heat of Thuringian glass increases rapidly with rise of temperature and proportionately with the latter between 0° and 100°. (2) The specific heats of sodium and potassium also increase considerably with rise of temperature, the increase being greater for sodium than for potassium (compare Behn, Abstr., 1900, ii, 259). The latent heat of fusion of potassium is 13·61, and that of sodium 17·75 calories. T. H. P.

Modified Gintl Pyknometer. M. RAKUSIN (*Chem. Zeit.*, 1905, 29, 1087).—A slight alteration of the pyknometer used by Gintl for taking the sp. gr. of semi-liquid or very soft fats or similar substances. The bottom of the glass cylinder holding the fat is removed and a movable bottom is provided. In this way it is easier to save the fat and to clean the apparatus. L. DE K.

Determination of Vapour Densities at High Temperatures.
III. Disintegration of Iridium by Carbon Dioxide. Dissociation of Carbon Dioxide. FRIEDRICH EMICH (*Monatsh.*, 1905, 26, 1011—1020. Compare Abstr., 1904, ii, 14; this vol., ii, 441; Holborn and Henning, Abstr., 1902, ii, 664).—Bunsen's method for the determination of vapour densities at high temperatures is applicable only to gas under relatively high pressures.

The author has determined the loss in weight (disintegration) of strips of iridium heated, in carbon dioxide and in nitrogen containing oxygen, by an electric current to various temperatures which were measured by means of a Holborn and Kurlbaum's optical pyrometer. No loss of weight occurs when iridium is heated in nitrogen or carbon monoxide. At 1500°, the loss of weight when iridium is heated in nitrogen containing 2·2 per cent. of oxygen is thirty times the loss in carbon dioxide, but at 1970° the loss in carbon dioxide and in nitrogen containing 2·2 per cent. of oxygen is approximately the same, whilst at 2150° the loss of weight in carbon dioxide is equal to the loss in nitrogen containing 5 per cent. of oxygen. The dissociation at various temperatures of carbon dioxide obtained from these results is compared with the dissociations calculated by Le Chatelier (Abstr., 1889, 205) and Trevor and Kortright (Abstr., 1895, ii, 211):

Temperatures.	Found. About	Percentage dissociation of carbon dioxide.	
		Le Chatelier.	Trevor and Kortright.
1500°	0·1	0·8	1
1970	4·5	4·0	8
2150	10·11	9·0	14

The disintegration of iridium in oxygen is due probably to the formation of an oxide which is volatile at high temperatures. G. Y.

Viscosity of Liquid Mixtures at their Boiling Points. ALEXANDER FINDLAY (*Chem. News*, 1905, 92, 206).—The viscosity of the binary mixtures benzene—carbon tetrachloride, benzene—alcohol, acetone—chloroform, and benzene—methyl alcohol, determined at their respective boiling points, in the hope that some relationship might be discovered between the viscosity composition-curve and the boiling point composition-curve, but this has been only partially realised.

D. A. L.

Influence of Phase Changes on the Tenacity of Ductile Metals at the Ordinary Temperature and at the Boiling Point of Liquid Air. GEORGE T. BEILBY and H. N. BEILBY (*Proc. Roy. Soc.*, 1905, A, 76, 462—468. Compare Abstr., 1904, ii, 647).—The observations recorded in the paper, which hardly lends itself to abstraction, are intended to prepare the way for a more direct attack on the problems of molecular cohesion.

J. C. P.

Equilibria between Solid and Liquid Phases in Ternary Systems which are Pseudo-binary. Explanation of Anomalous Fusion and Solution Phenomena. H. W.

BAKHUIS ROOZEBOOM and A. H. W. ATEN (*Zeit. physikal. Chem.*, 1905, **53**, 449—501).—A theoretical paper. J. C. P.

Ternary Equilibria. FRANS A. H. SCHREINEMAKERS (*Chem. Centr.*, 1905, ii, 1066; from *Chem. Weekblad*, **1**, 329—337).—The original paper consists of an introduction to the graphic method of representing equilibria in ternary systems and short descriptions of methods of investigation. E. W. W.

Equilibrium of the Electrolytic Dissociation of Partially Neutralised Acids and Bases. YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1904—5, **1**, 103—113. Compare Dawson, *Trans.*, 1903, **83**, 725).—It is shown that if a weak monobasic acid is half-neutralised by a strong monoacid base, the concentration of the hydrogen ions is equal to the dissociation constant of the acid and independent of the dilution of the solution. If a mixture of two weak monobasic acids in equivalent proportions is half neutralised by a strong monoacid base, the hydrogen ion concentration is equal to the square root of the product of the dissociation constants of the two acids. The conclusion is also reached that a solution of the acid salt of a dibasic acid, H_2A , may be considered as a half-neutralised mixture in equivalent proportions of the acids $H(HA)$ and HA . Similar relationships hold for partially neutralised weak bases. According to experiments of the author recorded previously on the bi-rotation of dextrose under the influence of ethylenediamine monohydrochloride, the velocity of the process increases with the concentration of the salt, whereas according to the above theoretical deductions it should be constant. These experiments have been repeated, and the different values for the velocity constant are now found to be more nearly equal. At dilutions of 400, 200, and 100 litres per mol., the values of the constant are 0.0126, 0.0147, and 0.0161 respectively. The mean value of the OH' concentration is calculated from these numbers to be 1.1×10^{-6} , and, utilising Bredig's number, 8.5×10^{-5} , for the dissociation constant of the first hydroxyl dissociation, the constant for the dissociation of the second hydroxyl is 1.4×10^{-8} . H. M. D.

Kinetics of Processes of Oxidation. ANTON SKRABAL (*Zeit. Elektrochem.*, 1905, **11**, 653—656).—As a guide to the mechanism of a reaction, the law of the primary formation of the least stable product is assumed. In cases of oxidation, this primary oxide is one which may decompose into a higher and a lower oxidation product. For example, sulphur dioxide, aldehyde, and hypiodous acid are the first products of oxidation of sulphur, alcohol, and hydriodic acid respectively. In homogeneous systems, the labile primary oxide is approximately in equilibrium both with the reacting materials and with the final products (Brunner, this vol, ii, 511). The fact that in cases of induced oxidation the quantity of induced oxidation bears a simple relationship to the quantity of primary oxidation leads the author to suppose that the intermediate oxide must always be very nearly in equilibrium with the final products of the reaction. In case the intermediate

oxide is formed by the first reaction too quickly to allow of the fulfilment of this condition, another, less stable, set of final products is formed.

The oxidation of oxalic acid by permanganate is taken as an example. Permanganate and oxalic acid react very slowly; complex manganic oxalate ions decompose at a measurable rate into manganous ions and carbon dioxide; permanganate and oxalic acid react very rapidly in presence of manganous ions. The slow decomposition of the complex manganic oxalate ions is ascribed to the action of manganic ions, formed by the dissociation of the complex ions, on oxalic acid. The very rapid reaction between permanganate, manganous ions, and oxalic acid is due to the primary formation of manganic ions from the manganous ions and permanganate. T. E.

Velocity of Decomposition of Nitrous Oxide. MATTHEW A. HUNTER (*Zeit. physikal. Chem.*, 1905, 53, 441—448).—Nitrous oxide was passed in a continuous current, at different rates in different experiments, through a porcelain tube heated electrically and kept at a high temperature. The extent to which the gas had decomposed during its passage through the hot tube was deduced from the density of the issuing gas, determined in a gas balance. Experiments were made at 713°, 805°, and 895°, and it was found that the course of decomposition is nearly that required for a bimolecular reaction. The influence of moisture on the rate of decomposition is not appreciable. The influence of temperature on the velocity-coefficient k is given by the equation $\log k = -31800/T + 24.12$.

It is shown that platinum electrodes are not polarised by nitrous oxide; a computation, however, makes it probable that the oxidation potential is about 0.39 volt higher than that of oxygen. J. C. P.

Mechanism of the Reaction by which γ -Hydroxy-acids are Converted into Lactones. BALTHASAR R. DE BRUYN (*Chem. Centr.*, 1905, ii, 1016; from *Chem. Weekblad*, 2, 557—563).—Whilst Henry's (Abstr., 1892, 1303) theory of the decomposition of γ -hydroxy-acids into lactones agrees with the facts, Visser's (this vol., ii, 571) appears to be quite irreconcilable with them. The formation of lactone follows the law of mass action. Since, at the concentration employed, 99 per cent. of the hydroxy-acid is not dissociated, the addition of an acid cannot have any appreciable effect on the dissociation. Visser's explanation does not account for the accelerating effect of strong acids or of the opposing influence of salts of hydroxy-acids. Henry's assumption of the catalytic action of the hydrogen ions, however, cannot be considered to afford a satisfactory explanation. E. W. W.

Control Experiments [over Long Periods of Time]. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1905, [viii], 6, 195—199).—Pure nitric acid remains colourless when kept in sealed tubes in the dark for seven years, and silver oxide moist or dry also remains unaltered under similar conditions. A mixture of 9 vols. of carbonic oxide and 6 vols. of oxygen either dry or moist undergoes no change when kept in sealed tubes for more than seven years.

Soils which have been sterilised and kept in closed vessels contain the same proportion of nitrogen at the end of twenty years as they did at the beginning (compare Abstr., 1886, 175 ; 1887, 395, 617).

M. A. W.

Absorption of Carbon Dioxide by Aqueous Salt Solutions and Binary Liquid Mixtures. A. CHRISTOFF (*Zeit. physikal. Chem.*, 1905, 53, 321—340).—The order of a number of salt solutions, arranged according to their ability to dissolve carbon dioxide, is in general the same as the order deduced from their absorptive power for other gases (compare Setschenoff, Abstr., 1889, 1044 ; Rothmund, Abstr., 1900, ii, 467). Solutions of alums dissolve carbon dioxide to about the same extent as the solutions of the simple sulphates which they contain. Solutions of the acid salts KHSO_3 , KHSO_4 , KH_2AsO_4 , KH_2PO_4 , K_2HAsO_4 , K_2HPO_4 , absorb less carbon dioxide than water does. The curves showing the variation of the solubility of carbon dioxide in binary mixtures with the composition of the mixtures may exhibit a minimum, as in the case of sulphuric acid and water, or a maximum, as in the case of acetic acid and carbon tetrachloride. The surface tension curve for these binary mixtures seems to exhibit a maximum where the solubility curve exhibits a minimum and *vice versa* (compare Skirrow, Abstr., 1902, ii, 600). The amount of carbon dioxide absorbed by solutions of borates and ortho- and metaphosphates is less than that calculated on the assumption that a whole molecule of hydrogen carbonate is formed from a molecule of the salt (compare Grünhut, Abstr., 1904, ii, 615).

J. C. P.

Velocity of Dissolution of Solid Substances. LUDWIK BRUNER and STANISLAW TOLLOCZKO (*J. Chim. phys.*, 1905, 3, 625—639).—It has been found by Noyes and Whitney that the velocity of dissolution of a solid in its own solution is given by the expression $dx/dt = C(S - x)$ where x is the concentration of the solution and S that of the saturated solutions (Abstr., 1897, ii, 479), and experiments of the authors confirmed this result (Abstr., 1904, ii, 117). Schürr has found, however, that S and x should be replaced by their logarithms, the expression of Noyes and Whitney being only valid, therefore, when the solubility is small (Abstr., 1904, ii, 543). The authors criticise Schürr's work, and have determined the velocity of solution in the case of sodium chloride. The method of working is described ; the results obtained are in complete accord with the law of Noyes and Whitney.

L. M. J.

Formation of Complexes: Hydration and Colour. FREDERICK G. DONNAN (*Zeit. physikal. Chem.*, 1905, 53, 317—320).—In reference to the papers by Lewis (this vol., ii, 509) and by Jones and Bassett (*ibid.*), it is shown how inadequately these authors interpret the colour changes exhibited by cobalt and copper salts in the light of modern theory and recent experimental work. In this connection, special reference is made to the views of Werner (Abstr., 1893, ii, 379) and of Aberg and Bodländer (Abstr., 1899, ii, 542), and to the work of Donnan and Bassett (Trans., 1902, 81, 939) and of Kohlschütter (Abstr., 1904, ii, 338). The application of these modern conceptions to

the interpretation of the relative colours of complex or double salts is attempted by the author for a number of cases in which cupric chloride or bromide is one constituent. Thus :

$\text{LiCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$	$\equiv [\text{Li}, 2\text{H}_2\text{O}]' [\text{Cu}, 3\text{Cl}]'$	is ruby-red ;
$\text{NH}_4\text{Cl}, \text{CuCl}_2$	$\equiv [\text{NH}_4]' [\text{Cu}, 3\text{Cl}]'$	is red ;
$\text{NH}_4\text{Cl}, \text{CuCl}_2, 2\text{H}_2\text{O}$	$\equiv [\text{NH}_4]' [\text{Cu}, 2\text{H}_2\text{O}, 3\text{Cl}]'$	is blue ;
$2\text{KCl}, \text{CuCl}_2, 2\text{H}_2\text{O}$	$\equiv [\text{K}]_2' [\text{Cu}, 2\text{H}_2\text{O}, 4\text{Cl}]'$	is blue ;
$\text{KCl}, \text{CuCl}_2$	$\equiv [\text{K}]' [\text{Cu}, 3\text{Cl}]'$	is brownish-red.
$\text{AgBr}, \text{HBr}, \text{CuBr}_2, 2\text{H}_2\text{O}$	$\equiv [\text{H}, 2\text{H}_2\text{O}]' [\text{Cu}, 3\text{Br}]'$	is brownish-red ;
$2\text{NH}_4\text{Br}, \text{CuBr}_2, 2\text{H}_2\text{O}$	$\equiv [\text{H}, \text{NH}_3]_2' [\text{Cu}, 2\text{H}_2\text{O}, 4\text{Br}]'$	is emerald-green ;
$\text{KBr}, \text{CuBr}_2$	$\equiv [\text{K}]' [\text{Cu}, 3\text{Br}]'$	is brownish-red ;
$2\text{LiBr}, \text{CuBr}_2, 6\text{H}_2\text{O}$	$\equiv [\text{Li}, 3\text{H}_2\text{O}]_2' [\text{Cu}, 4\text{Br}]''$	is brownish-red.

J. C. P.

Do Crystals Soften in the Neighbourhood of their Melting Point? N. SLATOWRATSKY and GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1905, 53, 341—348).—The plasticity of naphthalene and yellow phosphorus has been determined at various temperatures up to their melting points by a method previously described (*Ann. Physik*, 1902, 7, 198). The plasticity of ordinary samples of naphthalene increases markedly in the neighbourhood of the melting point, but this increase is largely due to the presence of impurities ; as these get pressed out and the crystals become chemically homogeneous, the plasticity falls off rapidly, and the temperature interval over which the naphthalene crystals appear to soften becomes much smaller. The question whether absolutely pure crystals would give any indication of softening has not been definitely answered.

J. C. P.

The Linear Force of Growing Crystals. GEORGE F. BECKER and ARTHUR L. DAY (*Proc. Washington Acad. Sci.*, 1905, 7, 283—288).—A weighted plate of glass was placed over a crystal of alum growing from solution. It was found that a crystal 1 cm. in diameter would raise a kilogram through a distance of several tenths of a millimetre. Similar results were obtained with other salts—copper sulphate, potassium ferrocyanide, and lead nitrate. The crystals grow with a cupped surface, and only a very narrow ring of material is in contact with the glass. The actual area of contact it was impossible to estimate, but it is so small that the force exerted by the growing crystal must amount to many pounds per square inch, being of the same order of magnitude as the resistance which the crystal offers to crushing stresses.

Attention is drawn to the geological importance of this force of crystallisation, especially in connection with the formation of quartz-veins and ore-deposits. If in quartz the force exerted during crystallisation on the walls of the vein is comparable with the resistance which the material offers to crushing, then it must be considerable.

L. J. S.

Theory of Dyeing. II. Quantitative Experiments on the Formation of Inorganic Analogues of the Substantive Dyes. WILHELM BILTZ and KURT UTSCHER (*Ber.*, 1905, 38, 2963—2973. Compare *Abstr.*, 1904, ii, 392 ; van Bemmelen, *Abstr.*, 1900, ii, 466).—Molybdenum-blue is obtained as a dark blue, amorphous mass when

a solution of molybdic acid, prepared by dissolving ammonium molybdate in the calculated quantity of dilute sulphuric acid, is reduced with hydrogen sulphide, freed from electrolytes by dialysis, and evaporated to dryness.

Comparative dyeing experiments have been carried out with cotton-wool and silk with molybdenum-blue, and with cotton-wool with vanadium pentoxide and benzopurpurin; the results are expressed in curves, which are drawn with the percentage of dye in the bath as abscissæ and the grams of dye absorbed by one gram of fibre as ordinates.

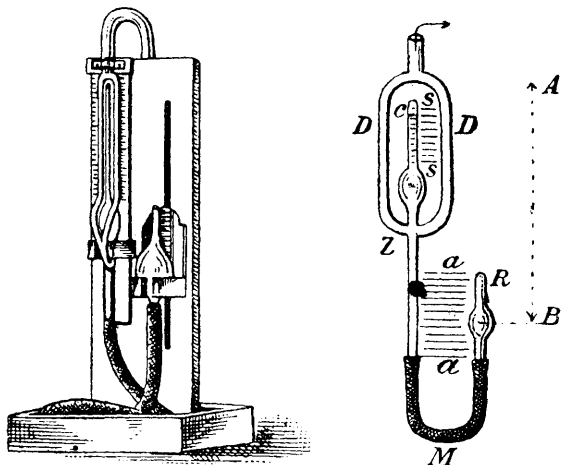
Similar absorption results are obtained with aluminium hydroxide and molybdenum-blue, colloidal silver, or benzopurpurin. G. Y.

Theory of Dyeing. III. State of Affinity of some Sulphur Dyes. WILHELM BILTZ and PAUL BEHRE (*Ber.*, 1905, 38, 2973—2977. Compare preceding abstract; *Abstr.*, 1904, ii, 324).—When dialysed for ten to fourteen days, solutions of "immedial" sulphur dyes in aqueous alkali sulphides form pure colloidal solutions, which, with the exception of the solution from "immedial yellow," are clear, and contain 0.096, 0.076, and 0.109 gram of immedial direct blue, bordeaux, and black respectively. These hydrosols resemble those previously investigated, especially in their capacity to form adsorption compounds. They are precipitated by electrolytes, are non-conductors of electricity, but under the influence of an *E.M.F.* of 110 vols. are attracted towards the anode, and therefore form adsorption compounds with positively charged hydrosols. Adsorption compounds are formed also with cotton-wool and aluminium, zirconium, ferric and stannic hydroxides.

G. Y.

Measurement of High Vacua in Chemical Distillation. HERMANN J. REIFF (*Chem. Centr.*, 1905, ii, 1065—1066; from *Chem. Zeitschr.*, 4, 426—427).—The glass tube, *R*, and the rubber tube, *M*, of the compression manometer, which is shown in the sketch, are filled with mercury. In order to estimate the total pressure under which a distillation at reduced pressure is being conducted, the upper end of the manometer is connected with the distilling apparatus, and the difference of level of the mercury in the tubes *MR* and *MZ* is read by means of the scale *a, a*. If *R* is now raised from *B* towards *A*, the mercury rises in the tubes *D, D* and in *c*, but, since *c* is closed at one end, the rising of the mercury in this tube is impeded by the air contained in it. The capillary tube, *c*, is graduated, so that the volume of the gas may be read to a small fraction of its original volume. The difference of level of the mercury in *D, D* and in *c* is read on the scale *s, s*, and corresponds with the pressure under which the air in *c* is confined. If the capillary tube, for example, is graduated to 1/10,000 of the total volume and an observation shows that a pressure of *m* mm. of mercury is required to compress the gas to *n*/10,000 of its original volume, then the pressure of the air is *mn*/10,000 mm. of mercury. From theoretical considerations, which are given in the original paper, it is shown that the pressure of the air which is read in this way is equal to that of the partial pressure

of the air in the distillation apparatus to which the manometer is attached, and is not affected by the saturated vapour or vapours which are present. If the first reading of the total pressure is G mm. and



the second reading of the partial pressure of the air is L mm., then the partial pressure of the vapour in the distilling apparatus is $G - L$ mm.
E. W. W.

Two Manometers of Great Sensitiveness for Small Pressures and a Gas Balance. E. GRIMSEHL (*Chem. Centr.*, 1905, ii, 941—942; from *Zeit. physikal.-chem. Unterr.*, 18, 198—202).—A sensitive manometer may be made of a U-shaped glass tube, both limbs of which terminate in bulbs. One limb contains coloured water and the other turpentine oil. When the former is connected with a gas under pressure by means of the side-tube which is fused on to the bulb, the water meniscus moves through an appreciable distance even when the pressure is small.

A similar manometer consists of two bulbs connected by a horizontal glass tube. To one bulb is attached a small glass tap and a side-tube. The apparatus contains a liquid, and in the horizontal tube there is a small bubble of air which is moved by a little pressure.

The gas balance consists of a long vertical tube to which a side-tube is attached at a point a short distance from the lower end. At the junction of these tubes there is a 3-way cock. The tube may be filled with gas by means of the side-tube, and the weight of the column of gas compared with a similar column of air by connecting the lower end of the vertical tube with either of the manometers described above.

E. W. W.

Causes why an Element often Passes from One Grade of Combination to another without giving rise to Intermediate Compounds. GEOFFREY MARTIN (*Chem. News*, 1905, 92, 185—187).—A theoretical paper. An element passes from one grade of com-

mination to another without giving rise to intermediate compounds when the latter are less stable under the conditions of experiment than the final product, and a relationship between this relative stability and valency is indicated.

D. A. L.

Gaseous Permeability of Vitreous Substances. Use in Chemistry, and Permeability, of Fused Silica Vessels. Permeability of Glass Vessels. Use of the Hot and Cold Tube in the Study of Chemical Reactions. MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1905, [viii], 6, 145—146, 146—164, 164—173, 174, 195).—A résumé of work already published (compare this vol., ii, 308, 316, 378, 386, 443).

M. A. W.

Chemical Lecture Experiments. JULIUS LANG (*Chem. Centr.*, 1905, ii, 948—949; from *Zeit. physikal.-chem. Unterr.*, 18, 202—206).—Simple lecture experiments are described which show (1) the preparation of sulphuric acid by the contact process, (2) the solidification of gases by means of liquid air, (3) the combustion of hydrogen in air or oxygen and the reversal of the flame, (4) the combustion of phosphorus in oxygen, the increase of weight of the phosphorus and the decrease of volume of the oxygen, and (5) the combustion of oxygen in hydrogen phosphide and of hydrogen phosphide in oxygen, and the reversal of the flame. In experiment (1), the sulphur trioxide is condensed in a test-tube surrounded by ice contained in an outer glass vessel. In experiment (2), the solidification of chlorine, hydrogen sulphide, sulphur dioxide, carbon dioxide, ethylene, acetylene, or cyanogen can be readily shown by means of the same condenser cooled by liquid air. The test-tube is in this case replaced by a Dewar tube. The combustion of hydrogen in oxygen, and oxygen in hydrogen, is also shown in the condenser, which in this case is cooled by water. In experiment (4), the flask in which the phosphorus is burnt in oxygen is connected with a graduated glass tube, the open end of which is placed in coloured water. In the last experiment, the gas evolved from calcium phosphide and water is in one case made to enter a cylinder containing oxygen, whilst in the other oxygen is led into a cylinder containing hydrogen phosphide.

E. W. W.

Inorganic Chemistry.

Determination of the Density of Chlorine at High Temperatures. MAX REINGANUM (*Chem. Centr.*, 1905, ii, 808; from *Physikal. Zeit.*, 6, 514—516).—The density of chlorine has been determined at high temperatures by means of an apparatus which consists of a small air thermometer with a vertical quartz capillary tube to which is connected a cooled air vessel with a bent delivery tube. By means of capillary tubes and 3-way cocks, the upper portion of the apparatus

may be filled with dry air and the lower with the gas to be examined. The vessel in which the air is collected is weighed. The apparatus is similar to Victor Meyer's, except that the volume of the dissociated gas is limited. The degree of dissociation is calculated from the difference between the results obtained for air and for the gas at the same temperature. The quartz vessel is heated by means of a Heraeus electric furnace. Since chlorine is liable to diffuse and escape, a temperature corresponding with a faint red heat is chosen for comparison instead of the ordinary temperature. At a temperature of 1137° , there was no evidence of the dissociation of chlorine.

E. W. W.

Distribution of Iodine between Two Solvents. YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1904—5, 1, 93—102. Compare Hantzsch and Vagt, *Abstr.*, 1902, ii, 8; Jakowkin, *Abstr.*, 1896, ii, 295).—By application of the law of mass action it is shown that the ratio of distribution of a substance between two phases must be constant and independent of the concentration, even when the dissolved substance combines with the solvent, provided the solutions are dilute. The explanations advanced to account for the variation of the ratio of distribution of iodine between different pairs of solvents with the concentration are shown to be improbable. To obtain further information, the distribution of iodine between aqueous alcohol and carbon disulphide was investigated at 25° , these two solvents being practically immiscible if the amount of alcohol present is less than 47.9 per cent. For a given alcohol-water mixture the ratio of distribution is independent of the iodine concentration and of the relative amounts of the two phases, and the variation of this ratio with the composition of the aqueous alcohol is given by the following numbers :

Grams of alcohol

in 100 c.c. of mixture	30.5	26.7	22.9	19.1	15.3	11.4	7.6
$(C_{\text{aq. alcohol}}/C_{\text{CS}_2}) \times 10^2$	1.29	0.76	0.49	0.34	0.28	0.23	0.20

The distribution data are compared with the data for the solubility of iodine in aqueous alcohol and carbon disulphide and the conclusion drawn that the ratios are very nearly identical.

H. M. D.

New Methods of Producing Ozone by means of Electricity. OSCAR KAUSCH (*Chem. Centr.*, 1905, ii, 806—807; from *Elektrochem. Zeit.*, 12, 91—96).—In Blockmarr and Wilford's apparatus, a wire is wound round the exterior of a cylinder of glass or other similar material and a second wire wound similarly on the inner surface, but in fewer coils. The wires are made the poles of the secondary circuit of an induction coil and the battery with which this is connected also works an electric fan by means of which air is forced through the tube. By sealing or partially closing the lower end of the glass tube, the pressure may be increased and the yield of ozone improved.

In Déchaux's apparatus, a large discharging surface is used in a small space and the temperature is kept low. A large number of ozonisers, each consisting of a glass tube fitted between two metal

tubes, are arranged in a box. The metallic tubes, which have a hexagonal or polygonal section and are fitted symmetrically about the glass tube, are connected with the poles of an electric machine and the inner tubes are cooled by means of a liquid. The air is dried and cooled before entering the apparatus.

The apparatus of the *Compagnie française de l'ozone* consists of a hermetically-sealed chest divided into two sections and containing a large number of systems of the type glass with tinfoil | air | metal | air | tinfoil with glass (Otto's system). The glass plates are connected to earth and all portions carefully insulated from one another. The air is cooled by means of liquid air.

In the apparatus of the *Ozon Maatschappij* in Amsterdam (Vosmaer's system) a condenser is inserted as a shunt in the secondary circuit of the transformer, and in the main circuit a self-induction coil. By raising the secondary *E.M.F.* by this means to a maximum, conditions favourable for the dark discharge are attained and when the distance of discharge is 13 mm. an *E.M.F.* of 9500 volts may be reached without any visible spark discharge. No dielectric is inserted between the electrodes.
E. W. W.

Action of Sodium Thiosulphate on Metallic Compounds in the Dry Way. FRANZ FAKTOR (*Chem. Centr.*, 1905, ii, 1218—1219; from *Pharm. Post.*, 38, 527—529. Compare *Abstr.*, 1905, ii, 452).—In the experiments from which the following conclusions have been deduced, a mixture of one part of the metallic compound with five of anhydrous sodium thiosulphate is strongly heated in a porcelain crucible and finally calcined. In the case of manganous chloride, sulphur and sulphur dioxide are evolved. The green residue gives off hydrogen sulphide when treated with hydrochloric acid and the solution formed by extracting with water and filtering contains sulphate, sulphide, and chloride. If the mixture is heated for 20 minutes after it has formed a uniform fused mass, the compound $\text{Na}_2\text{Mn}_3\text{S}_4$ is produced together with manganese sulphide, MnS . Silver nitrate, when mixed with sodium thiosulphate becomes yellow and brown, and on heating nitrous fumes are evolved. The black product contains silver sulphide and the aqueous extract sulphate and sulphide. Cadmium chloride gives a yellow mass which contains cadmium sulphide but not the compound NaCdS ; sulphate, sulphide, and chloride are present in the aqueous extract. Sulphur dioxide is evolved from the mixture with zinc oxide, and zinc sulphide is formed; the product is brown but becomes of a yellow colour on cooling. Black metallic lead sulphide is formed by the action of sodium thiosulphate on lead chloride.

When a mixture of five parts of sodium thiosulphate with one part of sodium chromate is heated, a brownish-red mass is formed which contains sulphate, sulphide, and sodium sulphochromite. When the sulphochromite is ignited, it forms the oxide Cr_2O_3 , and when dissolved in aqua regia it is oxidised to sulphochromate. By the action of silver nitrate or salts of lead, copper, or mercury (mercurous) on sodium sulphochromite, the corresponding salt of the metal is formed and the solution becomes green.

Molybdic acid and sodium thiosulphate yield the lustrous black sulphide, MoS_2 ; when the aqueous extract which contains thiomolybdate is acidified with sulphuric acid and boiled, the reddish-brown sulphide, MoS_3 , is formed. The mixture obtained by triturating sodium thiosulphate with tungsten trioxide is greenish-yellow and on ignition yields the sulphide WS_2 ; when the aqueous solution is acidified with hydrochloric acid and boiled, yellow tungstic acid, $\text{WO}_3 \cdot \text{H}_2\text{O}$, is precipitated.

When stannous chloride and sodium thiosulphate are rubbed together the mixture becomes bright brown and stannous sulphide is formed on ignition. Tin foil combines energetically with the sulphur of sodium thiosulphate, and arsenious and arsenic oxides yield the red disulphide and the yellow trisulphide respectively. Antimony oxide forms brown, greyish-black antimony sulphide, Sb_2S_3 .

Sodium iron sulphide, $\text{Na}_2\text{Fe}_2\text{S}_4$, obtained by heating four parts of sodium thiosulphate with one part of iron, forms dark green, needle-shaped crystals, but loses its crystalline structure on exposure to the air, becoming voluminous and finally forming a brownish-black powder which gives a dark green solution in water and evolves hydrogen sulphide when treated with hydrochloric acid. The same amorphous substance may also be prepared by melting sodium thiosulphate with iron at low temperatures. Sodium iron sulphide is insoluble in water and when heated forms the oxide; by the action of concentrated hydrochloric acid, hydrogen sulphide and sulphur are liberated, and when boiled with solutions of potassium cyanide, potassium ferrocyanide is formed. When anhydrous cobalt chloride is triturated with sodium thiosulphate, it becomes blue and then green and the black compound $\text{Na}_2\text{Co}_4\text{S}_6$ is formed on ignition. Anhydrous nickel chloride turns brownish-green; sulphur dioxide and sulphur are liberated on heating and the product has a composition corresponding with the formula $\text{Na}_2\text{Ni}_2\text{S}_3$. At low temperatures, the product is black and has the empirical composition $\text{Na}_2\text{Ni}_4\text{S}_{10}$. Cupric chloride yields sulphur, sulphur dioxide, and black cuprous sulphide, and mercuric chloride, sulphur, sulphur dioxide, and black amorphous sulphide, HgS . Cinnabar is converted into the black sulphide when ignited with sodium thiosulphate, and a black sublimate is also formed which becomes red when rubbed. Bismuth chloride forms slender, grey needles of the compound $\text{Na}_2\text{Bi}_2\text{S}_4$, and thallium sulphate a brick-red product which is rapidly converted into the brown sulphide, Tl_4S_5 , on exposure to air. Sulphide and sulphate are formed by the action of magnesium powder on sodium thiosulphate and bright yellow aluminium sulphide is obtained from alumina.

E. W. W.

Reduction of Trithionates to Sulphites by Arsenite and Stannite. AUGUST GUTMANN (*Ber.*, 1905, 38, 3277—3281. Compare this vol., ii, 384).—Sodium trithionate is reduced to sodium sulphite by sodium arsenite in sodium hydroxide solution; the amounts of arsenate and thioarsenate formed agree with those required by the equation $\text{Na}_2\text{S}_3\text{O}_6 + 2\text{Na}_3\text{AsO}_3 + 2\text{NaOH} = 2\text{Na}_2\text{SO}_3 + \text{Na}_3\text{AsSO}_3 + \text{Na}_3\text{AsO}_4 + \text{H}_2\text{O}$. Sodium trithionate is reduced by sodium stannite and hydroxide to sodium sulphite, stannate, and thiostannate. Sodium

dithionate is not reduced by sodium arsenite or stannate solution at the laboratory temperature or at the boiling point. G. Y.

Preparation of Stable, Dry Hyposulphites. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 160529).—Water is readily removed from metallic hyposulphites by means of methyl or ethyl alcohol, acetone, or ethyl acetate. In presence of such liquids, sodium hyposulphite may be heated to 100° and the sodium zinc salt still more strongly without decomposition. The solid is made into a paste with one of these liquids, washed, drained, and dried at 70° . The washing liquid is dehydrated by means of lime or a similar agent, distilled, and again employed. In the case of the sodium salt, the final product contains 96—98 per cent. of pure hyposulphite. C. H. D.

Direct Synthesis of Ammonia. EDGAR P. PERMAN (*Proc. Roy. Soc.*, 1905, A, 76, 167—174. Compare *Proc. Roy. Soc.*, 1904, 74, 110; also Hemptinne, *Abstr.*, 1902, ii, 450; Haber and van Oordt, this vol., ii, 159).—Ammonia cannot be synthesised by heat alone, and the decomposition of ammonia by heat may accordingly be regarded as a non-reversible reaction. Ammonia may be synthesised in small quantities, (a) by heating with metals, iron for example; (b) by exploding with oxygen; (c) by sparking. These are reversible reactions. The synthesis of ammonia is apparently affected only when the gases are ionised. Metals which readily form nitrides (magnesium, for example) do not promote the synthesis of ammonia to a greater extent than other metals, hence it appears that the nitrides are not an intermediate stage in the formation of ammonia. J. C. P.

Formation of Ammonia from its Elements. FRITZ HABER and G. VAN OORDT (*Zeit. anorg. Chem.*, 1905, 47, 42—44. Compare this vol., ii, 159).—Perman's criticism (*Proc. Roy. Soc.*, 1905, A, 76, 169) is shown to be inapplicable to the authors' work. D. H. J.

Action of Nitrogen on Water-vapour at High Temperatures. OLIN F. TOWER (*Ber.*, 1905, 38, 2945—2952; *J. Amer. Chem. Soc.*, 1905, 27, 1209—1216).—Nitrogen saturated with water-vapour was passed through a glass globe in which it was subjected to the action of sparks from a large induction coil, and the amount of hydrogen and nitric acid formed was determined.

In a further series of experiments, the nitrogen—water-vapour mixture was passed through an electrically heated Nernst iridium furnace. The gases issuing from the furnace were passed through a tube containing concentrated sulphuric acid, mixed with oxygen to oxidise the nitric oxide, and finally passed through a second sulphuric acid tube. The reaction $N_2 + 2H_2O = 2NO + 2H_2$ was studied in this way at 2000° .

The interaction of nitrogen and water-vapour takes place extremely slowly; an equilibrium is reached probably when 4 c.c. of nitric oxide are present per litre, whilst the amount calculated from the dissociation of water-vapour and the equilibrium between nitrogen, oxygen, and nitric oxide is 3.3 c.c. G. Y.

Constitution of Nitric Acid and its Hydrates. W. NOEL HARTLEY (*Proc. Roy. Dublin Soc.*, 1905, [ii], 10, 373—377).—The author's previous work (*Trans.*, 1903, 85, 658) had indicated the probable existence of the acid $\text{H}_3\text{NO}_4 \cdot \text{H}_2\text{O}$, and he now points out the agreement of his results and of those of Veley and Manley (*Abstr.*, 1902, ii, 135) with the demonstration by Erdmann of the existence of orthonitric acid and other polybasic nitric acids (*Abstr.*, 1903, ii, 73).
L. M. J.

Explosions of Mixtures of Coal Gas and Air in a Closed Vessel. LEONARD BAIRSTOW and A. D. ALEXANDER (*Proc. Roy. Soc.*, 1905, A, 76, 340—349).—Mixtures of coal-gas and air are not inflammable until the volume of coal-gas is greater than one-seventeenth of the total volume. Only a small fraction of the gas then burns, but this fraction rapidly increases as the mixture becomes richer, until the coal-gas is one-twelfth of the total volume. The least inflammable of the constituents then burns, and combustion remains complete so long as air is in excess. In the latter cases it is still probable that the constituents burn successively and not simultaneously. The hypothesis of a specific heat increasing with temperature is not supported by direct experiment. The difference between the pressures calculated for explosions in a closed vessel and those actually obtained is probably due to the partial decomposition of both steam and carbon dioxide demonstrated by Deville.
J. C. P.

Variations in the Amount of Carbon Dioxide in the Air of Kew during the Years 1898—1901. HORACE T. BROWN and FERGUSSON ESCOMBE (*Proc. Roy. Soc.*, 1905, B 76, 118—121).—The average of 91 experiments gave 2.94 volumes of carbon dioxide in 10,000 of air, the lowest value being 2.43, and the highest (obtained during a fog) 3.60. The proportion is, as a rule, somewhat greater during the winter than during the summer, but the variations probably depend more on anticyclonic than on seasonal conditions.

Reference is made to the importance of these variations for plant nutrition, since it has been shown that, within fairly wide limits, the rate of assimilation is proportional to the partial pressure of the carbon dioxide.
G. S.

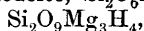
Atomic Weight of Silicon. II. JULIUS MEYER (*Zeit. anorg. Chem.*, 1905, 47, 45—55).—Jordis has privately drawn the author's attention to the fact that the method of determining the atomic weight of silicon employed by the latter, decomposition of silicon tetrachloride with cold water and ignition to silicon dioxide (this vol., ii, 246), might be inaccurate owing to the obstinate retention of a small amount of hydrogen chloride in chemical combination with the silica, even after long ignition (compare Jordis and Kanter, *Abstr.*, 1903, ii, 475). In the present paper, the retention of a small amount of hydrogen chloride by the silica when the ignition is carried out at a low temperature is confirmed; conductivity measurements showed, however, that it is not chemically combined with the silica, as had been supposed, but is retained by absorption. When, on the other hand,

the ignition is carried out at 1000° for three or four hours, the amount of hydrogen chloride retained is quite inappreciable. Since the results given in the former paper were obtained by ignition at 1000° until the weight was constant (often for five or six hours), the objection does not apply.

Employing the new value for chlorine, 35.47, found by Richards and Wells (this vol., ii, 450), the value $\text{Si} = 28.25$ ($\text{O} = 16$) is obtained from the results given in the previous paper. G. S.

Decomposition of Silicon. THEODOR GROSS (*Chem. Centr.*, 1905, ii, 953; from *Elektrochem. Zeit.*, 12, 48—50).—When an alkaline solution of potassium silicate was electrolysed by means of an alternating current between electrodes of silver containing a small quantity of copper, the evolution of gas ceased after an hour and no further decomposition occurred. The solution was found to have lost up to 20 per cent. of silica. The residue contained a new substance which could not be further decomposed. After fusing with sodium potassium carbonate, a pinkish-white residue remained, the weight of which was equal to about 14 per cent. of the silica which had disappeared. This substance was only partially soluble in hydrofluoric acid, almost insoluble in hydrochloric acid, and quite so in water or nitric acid; when fused with a large quantity of potassium hydroxide, the product was completely soluble in dilute hydrochloric acid. The hydrochloric acid solution gave a precipitate with potassium hydroxide, which was not soluble in excess of the alkali. When silica or flint was dissolved in molten alkali and the solution submitted to the action of an alternating current, a similar substance was obtained. The author concludes that silicon is partially decomposed and supposes that carbon is one of the constituents. E. W. W.

Preparation of Silicic Acids by the Decomposition of Natural Silicates. GUSTAV TSCHERMAK (*Zeit. physikal. Chem.*, 1905, 53, 349—367).—Various silicic acids have been obtained by digesting natural silicates with dilute or strong hydrochloric acid for a considerable time at a temperature generally below 60° . The product was carefully washed by decantation and then placed in an open dish with sufficient water to cover it. The loss of weight of this dish was determined regularly at intervals of twenty-four hours, and the point at which all mechanically-held water was given off could thus be determined, for the rate at which the chemically combined water is given off is much less. At the point just referred to, the loss on ignition of the silicic acid was determined, and the composition of the latter thus ascertained. By this method, it has been shown that natrolite, $\text{Si}_3\text{O}_{12}\text{Al}_2\text{Na}_2\text{H}_4$, diopside, SiO_4CuH_2 , and zinc silicate, $\text{SiO}_5\text{Zn}_2\text{H}_2$, are derivatives of orthosilicic acid, SiO_4H_4 . Anorthite, $\text{Si}_2\text{O}_8\text{Al}_2\text{Ca}$, is a derivative of metasilicic acid, SiO_3H_2 . Leucite, $\text{Si}_2\text{O}_6\text{AlK}$, and serpentine,



are derivatives of what is termed "leucite" acid, $\text{Si}_2\text{O}_6\text{H}_4$. Grossular, $\text{Si}_3\text{O}_{12}\text{Al}_2\text{Ca}_3$, epidote, $\text{Si}_3\text{O}_{13}\text{Al}_3\text{Ca}_2\text{H}$, zoisite, $\text{Si}_3\text{O}_{13}\text{Al}_3\text{Ca}_2\text{H}$, prehnite, $\text{Si}_3\text{O}_{12}\text{Al}_2\text{Ca}_2\text{H}_2$, are derivatives of "garnet" acid, $\text{Si}_3\text{O}_8\text{H}_4$.

Albite, $\text{Si}_3\text{O}_5\text{AlNa}$, is a derivative of "albite" acid, $\text{Si}_3\text{O}_7\text{H}_2$. The densities of these five silicic acids are, respectively, 1.576, 1.813, 1.809, 1.910, and 2.043. The various acids behave differently towards methylene-blue, and it is found that the strength of coloration produced diminishes as the number of hydroxyl groups (relatively to silicon) falls off.

J. C. P.

Determination of the Amounts of Neon and Helium in Atmospheric Air. Sir WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1905, A, 76, 111—114. Compare Abstr., 1903, ii, 476).—Dewar's method of using cooled cocoanut charcoal as an absorbent for gases has made it easy to carry out the determination, for at -100° air is readily absorbed by such charcoal, whilst neither helium nor neon is absorbed in appreciable quantity. Further, at the temperature of liquid air, neon is retained by charcoal in considerable quantity, whilst helium is not so retained. Working on the basis of these observations, the author finds that the percentage of neon in gaseous air is 0.0000086 by weight and 0.0000123 by volume, the percentage of helium being 0.00000056 by weight and 0.0000040 by volume. The experiments indicate also that the amount of free hydrogen in air must be less than 1/500th of the volume of neon and helium together.

J. C. P.

Electric Preparation of Colloidal Metals. THE SVEDBERG (*Ber.*, 1905, 38, 3616—3620. Compare Bredig, Abstr., 1900, ii, 213; Billitzer, *ibid.*, 1902, ii, 454; Blake, *Amer. J. of Sci.*, 1903, 16, 431).—Colloidal solutions of metals cannot be obtained by Bredig's method when organic solvents are used, as considerable quantities of carbon are always deposited. Blake's method gives negative results with ether, chloroform, benzene, or acetone.

Colloidal solutions of metals in organic solvents have been obtained by suspending the metal in the form of thin foil and using electrodes of iron or aluminium with a potential difference of 110 volts and a current density so small that it can scarcely be measured by an ordinary ammeter. Tin, gold, silver, and lead have been obtained in a colloidal state in various organic solvents, but extremely hard metals such as aluminium cannot be disintegrated by this method.

A second method consists in connecting a glass condenser of 225 sq. cm. surface with the induction coil and attaching the secondary poles to the electrodes, which are immersed in the liquid contained in a porcelain dish. The metal is used in a granular form or as wire clippings. When the current is passed, sparks play between the metal particles, and in the course of a few minutes dark-coloured solutions are obtained. These contain no large particles and hence need not be filtered. Colloidal solutions of magnesium, zinc, aluminium, tin, antimony, iron, nickel, and even alkali metals in ether have been obtained.

The solutions of sodium are violet and those of potassium bluish-violet in colour, and these facts are used to support Elster and Geitel's view that the colorations produced by cathode or Tesla rays on alkali chlorides are due to colloidal solutions of the metal in the alkali chloride.

J. J. S.

Boiling Points of the Alkali Metals. OTTO RUFF and OTTO JOHANNSEN (*Ber.*, 1905, 38, 3601—3604. Compare Carnelley and Williams, *Trans.*, 1879, 35, 563; Perman, *Trans.*, 1889, 55, 326).—The authors have determined the boiling points of the alkali metals in a wrought iron distilling apparatus, which, contrary to previous statements, is not attacked. The temperatures were observed by means of a platinum—platino-rhodium thermo-element. The following boiling points under 760 mm. pressure are accurate to within $\pm 5^\circ$: caesium, 670° ; rubidium, 696° (698.5°); potassium, 757.5° (759°); sodium, 877.5° (879°). The temperatures in brackets are the highest observed on rapid boiling of the metals.

Lithium was prepared by electrolytic fusion of a mixture of lithium and potassium chlorides in Muthmann, Hofer, and Weiss' apparatus (*Abstr.*, 1902, ii, 262), the current density being about 85 amperes with an *E.M.F.* of 20 volts. At about 1400° , half of the lithium in the distillation apparatus remained unchanged, the rest being converted into hydride or nitride, and complete volatilisation did not take place even at the melting point of the wrought iron vessel. The boiling point of lithium must be above 1400° .

A curve drawn with the atomic weights of these metals as abscissae, and their boiling points as ordinates resembles the melting-point curve but does not permit of the boiling points being represented as a simple function of the atomic weights. G. Y.

Some Reactions of the Alkali and Alkaline-earth Hydrides. Influence of Traces of Moisture on the Decomposition of the Alkali Hydrides by Carbon Dioxide or Acetylene. HENRI MOISSAN (*Ann. Chim. Phys.*, 1905, [viii], 6, 289—322, 323—333).—A *résumé* of work already published (compare *Abstr.*, 1902, i, 253, 255; ii, 136, 206; 1903, i, 595, 785; ii, 349, 365, 367; this vol., i, 507). M. A. W.

Potassium Percarbonate. WILLIAM D. BROWN (*J. Amer. Chem. Soc.*, 1905, 27, 1222—1224).—The degree of purity of specimens of potassium percarbonate (Constam and Hansen, *Abstr.*, 1897, ii, 550) can be determined by titration with potassium permanganate in a solution acidified with sulphuric acid, when the following reaction takes place: $5\text{K}_2\text{C}_2\text{O}_6 + 8\text{H}_2\text{SO}_4 + 2\text{KMnO}_4 = 2\text{MnSO}_4 + 6\text{K}_2\text{SO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2 + 5\text{O}_2$.

Samples of the salt were prepared and found to contain only 30—40 per cent. of the percarbonate, whereas Hansen (*Abstr.*, 1898, ii, 23) obtained a product containing 80—95 per cent. A comparison of the reactions of potassium percarbonate with those of sodium peroxide shows that the latter is to be preferred as an oxidising agent.

E. G.

Potassium Chromates. FRANS A. H. SCHREINEMAKERS (*Chem. Centr.*, 1905, ii, 1067; from *Chem. Weekblad*, 1, 837—848. Compare Jaeger and Krüss, *Abstr.*, 1889, 1117).—Potassium trichromate, $\text{K}_2\text{Cr}_3\text{O}_{10}$, and potassium tetrachromate, $\text{K}_2\text{Cr}_4\text{O}_{13}$, may be prepared by adding chromic acid to the chromate or dichromate. The conditions

of equilibrium of the system—potassium oxide, water, and chromic acid at 30° have been investigated. The compounds which separate in a solid form correspond with those obtained in the case of ammonium chromates (this vol., ii, 820), except that when no chromic acid is present the hydrate $\text{KOH} \cdot 2\text{H}_2\text{O}$ is deposited from a solution which contains about 55 per cent. of potassium hydroxide and 45 of water. At 30° , 100 grams of water dissolve 64.91 of potassium chromate and 18.12 of dichromate; it is impossible, therefore, to precipitate the chromate from a solution of dichromate by the addition of a base, but the corresponding dichromate may be precipitated from a solution of potassium or ammonium chromate by the addition of chromic acid. A chromate containing more potassium than potassium chromate cannot exist at 30° , and the conditions under which the trichromate is stable are rather limited. A higher chromate than the tetrachromate does not exist at 30° in conjunction with its saturated solution. Potassium tri- and tetra-chromates are decomposed by water, forming dichromate.

E. W. W.

Electrolytic Preparation of Sodium. KONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 160540).—In the electrolysis of fused sodium chloride, a considerable quantity of metallic sodium dissolves in the bath, and at the high temperature required for fusion is lost by burning. This is avoided by using as an electrolyte a mixture of sodium chloride with potassium fluoride, the former in large excess. In place of potassium fluoride, a mixture of sodium fluoride and potassium chloride may be added. The temperature of fusion is thus lowered.

C. H. D.

Physical Properties of Sodium Vapour. P. V. BEVAN (*Proc. Camb. Phil. Soc.*, 1905, 13, 129—131).—Wood has previously observed that sodium vapour appears to possess considerable cohesion and frequently exhibits a free surface (*Phil. Mag.*, 1904, [vi], 8, 296). The formation of a cloud of sodium vapour is easily observed by heating a piece of sodium in a partially exhausted tube and observing through the tube a Bunsen flame coloured by sodium. The cloud possesses a definite boundary if the pressure of the gas in the tube is sufficiently high, but in a high vacuum no cloud is observed. In perfectly dry hydrogen also no cloud is formed. It was found that distinct distillation of sodium takes place at 100° , that is, 2° above its melting point.

L. M. J.

Preparation of Alkali Nitrites. JACOB GROSSMANN (D.R.-P. 160671).—In the reduction of sodium nitrate by carbon according to the equation $2\text{NaNO}_3 + 2\text{NaOH} + \text{C} = 2\text{NaNO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$, nearly one-half of the sodium nitrate is lost by further reduction when the carbon is employed in the amorphous form. When, however, natural graphite is employed in place of coke, and an oxide or hydroxide of an alkaline-earth in place of sodium hydroxide, this loss is avoided, and a lower temperature suffices for the reduction.

C. H. D.

Ammonium Chromates. FRANS A. H. SCHREINEMAKERS (*Chem. Centr.*, 1905, ii, 1066—1067; from *Chem. Weekblad*, 1, 395—410. Compare Jaeger and Krüss, *Abstr.*, 1889, 1117).—The conditions of equilibrium of systems consisting of ammonia, chromic acid, and water at 30° have been investigated. The following compounds separate in the solid state in the order given: ammonium chromate and dichromate, dichromate, dichromate and trichromate, trichromate, trichromate and tetrachromate, tetrachromate and chromic acid, chromic acid. Ammonium chromate cannot be dried at 100° without decomposing, and even at lower temperatures it gives off ammonia and forms dichromate. The chromate and dichromate are not decomposed by dissolving in water, but the tri- and tetra-chromates are. Chromates containing more ammonia than ammonium chromate are not formed even at 0°; the chromate is the only compound which separates in a solid form at 0° from solutions containing about 1.5 per cent. of chromic acid and about 42 of ammonia. At 30°, 100 grams of water dissolve 47.17 of dichromate, about 40.4 of chromate, and 165.1 of chromic acid. The whole series of chromates may be prepared by adding chromic acid to the chromate. E. W. W.

Reaction between Silver Nitrate and Disodium Hydrogen Phosphate. YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1904—5, 1, 158—167. Compare Berthelot, *Abstr.*, 1901, ii, 503).—The influence of the concentration and of the relative proportions in the reaction between silver nitrate and disodium hydrogen phosphate at 25° has been studied. When the two substances are mixed in equivalent proportions, the percentage of the silver precipitate increases slightly with the concentration. Within the limits represented by 0.005 and 0.120 mol. AgNO_3 per litre, the percentages are 51.8 and 59.0 respectively. Solubility experiments indicate that the concentration of the silver remaining in the solution is the same as that in a saturated solution of nitric acid of which the concentration is equal to the concentration of the acidic hydrogen in the former. The following solubility data were obtained.

Concentration of nitric acid.								Mols. per litre
0.005	0.01	0.015	0.02	0.025	0.03	0.035	0.04	
Concentration of silver in solution.								Mols. per litre
0.00748	0.0142	0.0206	0.0263	0.0325	0.0387	0.0434	0.0494	

Assuming that the solutions contain principally silver nitrate, silver dihydrogen phosphate, and free phosphoric acid together with their dissociation products, the equilibrium condition has been deduced and this is shown to be satisfied by the experimental data for varying dilution and varying relative proportion of the reacting substances. The influence of an excess of silver nitrate in increasing the amount of precipitated silver phosphate is small, and this increase is very nearly proportional to the excess of silver nitrate added. On the other hand, the influence of an excess of disodium hydrogen phosphate is very considerable and the precipitation of the silver is practically complete when three equivalents of disodium hydrogen

phosphate are added to one equivalent of silver nitrate. This result also agrees with the theoretical relationship deduced. H. M. D.

Equilibrium among Certain Bases in Simultaneous Contact with Phosphoric Acid. ANTONIO QUARTAROLI (*Gazzetta*, 1905, 35, ii, 290—304).—On saturating one mol. of phosphoric acid with an equivalent of lime (or baryta) and two equivalents of sodium (or potassium) hydroxide, precipitation of two-thirds of the phosphoric acid with formation of the double salt, $\text{Ca}_3\text{Na}_6(\text{PO}_4)_4$ or $\text{Ba}_3\text{Na}_6(\text{PO}_4)_4$ [which Berthelot (*Abstr.*, 1901, ii, 504) stated to occur] does not take place, scarcely one-third of the phosphoric acid being precipitated in the form of tri- and tetra-basic phosphates. Two-thirds of the phosphoric acid remains in solution as tri- and di-basic phosphates. Hence, bases added in equivalent quantities to phosphoric acid distribute themselves unequally between the solution and the precipitate, and, as the latter is partly composed of tetrabasic phosphates, the solution must contain a certain amount of dibasic phosphates. An exception to this is met with when a solution of phosphoric acid containing one equivalent of baryta and two equivalents of sodium hydroxide is left for a long time; one atom of sodium and one of barium (less than was calculated by Berthelot) then pass into the insoluble condition and precipitate a little less than half of the phosphoric acid.

Nor when one mol. of phosphoric acid is saturated with one equivalent each of lime (or baryta) and sodium (or potassium) hydroxide is it found that two-thirds of the phosphoric acid is precipitated with formation of insoluble double phosphates containing equivalent quantities of calcium and sodium. In this case, too, the bases are unequally distributed between the precipitate and the solution, the latter containing mono- and di-basic phosphates and the former di- and tri-basic, and in some cases tetra-basic phosphates.

Magnesia exhibits a behaviour which is different from that of lime or baryta and which varies markedly with the alkali present. Thus, on adding one equivalent of magnesia and two equivalents of sodium hydroxide to one mol. of phosphoric acid, only magnesium is precipitated, whilst if the sodium hydroxide is replaced by potassium hydroxide, a portion of the latter passes into the insoluble state. On adding one equivalent of sodium or potassium hydroxide to monomagnesium phosphate, the amount of phosphoric acid precipitated is much less than in the other cases and only amounts to about one-sixth of the total quantity; seeing that dimagnesium phosphate, like the dicalcium salt, is only very slightly soluble and that the alkali hydroxide present is sufficient to precipitate it, it is probable that soluble double phosphates are formed. T. H. P.

Solubility of Barium Sulphite in Water and in [Sucrose] Solutions. JOHANN ROGOWICZ (*Zeit. Ver. Deut. Zucker-Ind.*, 1905, 596, 938—940).—The results of the author's measurements, in grams of barium sulphite present in 100 c.c. of solution, are given in the following table:

	20°.	80°.
Water.....	0·01974	0·00177
Sucrose solution, 10° Brix	0·01040	0·00335
" " 20 " 	0·00968	0·00289
" " 30 " 	0·00782	0·00223
" " 40 " 	0·00484	0·00158
" " 50 " 	0·00298	0·00149
" " 66 " (saturated) ...	0·00223	0 00112

T. H. P.

The Molecular Weight of Mercuric Silver Iodide. WALTER HERZ and M. KNOCH (*Zeit. anorg. Chem.*, 1905, **46**, 460).—The molecular weight of the double iodide has been determined in alcoholic solution by the boiling-point method and found = 428. The theoretical value for $\text{HgI}_2 = 453\cdot9$. Hence the salt is undissociated and unimolecular in alcoholic solution.

D. H. J.

Manganese-Iron Alloys. MAX LEVIN and GUSTAV TAMMANN (*Zeit. anorg. Chem.*, 1905, **47**, 136—144).—The freezing-point curve indicates the absence of any compound of iron and manganese; there exists an unbroken series of mixed crystals of the two metals. This result is only apparently opposed to the microscopic appearance of the alloys; under the microscope, there appear to be in some cases two structural elements, but this is due to the fact that during rapid cooling equilibrium is not at once established between the liquid alloy and the mixed crystals, and crystals richer in iron separate first and then become surrounded by others, richer in manganese. The melting point of manganese is 1247° , of iron 1551° . Preliminary experiments to ascertain the temperatures at which the magnetic permeability of manganese-iron alloys abruptly change, gave the following results:

Percentage of iron	100	90	80
Disappearance	950°	820°	750°
Return	750°	715°	720°

D. H. J.

Reduction of Oxides, a New Method of preparing the Binary Compound, SiMn_2 , by means of Aluminium. ÉMILE VIGOUROUX (*Compt. rend.*, 1905, **141**, 722—724. Compare Abstr., 1896, ii, 362).—By firing a mixture of silica, manganese oxide, and aluminium, and allowing the flux to cool very slowly, a brittle mass is obtained which, after extraction with dilute hydrochloric acid and then with dilute hydrofluoric acid, consists of crystals of the manganese silicide, SiMn_2 , which is decomposed by the action of warm hydrochloric or nitric acid, and in this respect differs from the compound of the same composition described by Lebeau (compare Abstr., 1903, ii, 215). Attempts to prepare a silicide containing a higher proportion of manganese than the one described above were not successful.

M. A. W.

Conditions of Stability of Certain Suspensions. FEDERICO GIOLITTI (*Gazzetta*, 1905, 35, ii, 181—192).—The author has made a number of experiments on the coagulation of colloidal ferric hydroxide solution, prepared by boiling freshly-prepared ferric acetate solution until acid vapours are no longer evolved. A gelatinous hydrogel is formed by the addition to this solution of a small quantity of sulphuric, sulphurous, selenious, iodic, periodic, boric, or phosphoric acid, or of certain salts. The addition of a small amount of hydrochloric, hydrobromic, hydriodic, nitric, perchloric, or perbromic acid to the colloidal solution causes slight precipitation of a finely-divided, brick-red powder which cannot be removed by filtration, is soluble in water, and is obtained in larger quantity if the amount of acid added is increased. The acids given in the first of the above two groups all act with about equal rapidity, even when present in only very small amounts. With those of the second group, it is possible to state limits of concentration between which they are capable of completely precipitating the ferric hydroxide; in this case, too, the precipitate obtained has all the properties of the hydrogel, whilst the acids of the first group yield a precipitate with altered properties.

A solution of ferric hydroxide produced by the dialysis of a solution of ferric chloride saturated with freshly-precipitated ferric hydroxide exhibits less regularity in its behaviour, the amount of the precipitate, for example, increasing gradually with the amount of acid added.

Other colloidal solutions exhibit properties similar to those observed with ferric hydroxide solution. T. H. P.

Constitution and Genesis of Iron Sulphates: Synthesis of Sodium Ferric Sulphates. RUDOLF SCHARIZER (*Zeit. Kryst. Min.*, 1905, 41, 209—225).—The greenish-white ferrinatrite (=ferro-natrite), $\text{Na}_3\text{Fe}_2\text{S}_6\text{O}_{24}\cdot 6\text{H}_2\text{O}$, and the orange-yellow sideronatrite, $\text{Na}_4\text{Fe}_2\text{S}_4\text{O}_{17}\cdot 7\text{H}_2\text{O}$, both of which are from Chili, are considered to be derivatives of the acid ferric sulphate, $\text{Fe}_2(\text{OH})_2(\text{SO}_4\text{H})_4\cdot 6\text{H}_2\text{O}$, and to have the constitutional formulæ $\text{Fe}_2(\text{SO}_4\text{Na})_6\cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2(\text{OH})_2(\text{SO}_4\text{Na})_4\cdot 6\text{H}_2\text{O}$ respectively.

Ferrinatrite is obtained artificially by allowing a mixture of acid ferric sulphate and acid sodium sulphate to remain in a moist atmosphere for several months. The greenish-white crystallised product is hexagonal, and has the composition given above; it loses all its water at 100° .

Sideronatrite is obtained as indistinct (orthorhombic?) crystals by the slow evaporation of a solution containing ferric and sodium sulphates and sulphuric acid, but if allowed to remain in contact with the solution it soon changes to ferrinatrite. It is also deposited from a solution of ferrinatrite, or when a solution of acid sodium sulphate acts on ferric hydroxide. Six-sevenths of the water of artificial sideronatrite is lost at 125° , the remaining molecule being expelled only at a high temperature. L. J. S.

Higher Oxide of Nickel. ITALO BELLUCCI and E. CLAVARI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 234—242).—Experiments on the oxidation of nickel sulphate in alkaline solution by means of various

oxidising agents and under various conditions of temperature and dilution lead to the following conclusions: (1) Any one oxidising agent yields, both at the ordinary temperature and on heating, products giving the same value for the ratio nickel:oxygen, but at 0° the proportion of oxygen is much higher. (2) The degree of oxidation of the nickel depends on the nature of the oxidising agent and on the rapidity of the oxidation, the lowest numbers being obtained when the precipitate is left for a long time in contact with excess of the oxidising solution. (3) None of the oxidising agents employed led to the formation of an oxide having the formula Ni_2O_3 . (4) On oxidation with bromine in presence of excess of potassium carbonate at 0° and washing the precipitate with concentrated potassium carbonate solution, the ratio of nickel to oxygen was found to have the value 10:19.07; this is in good agreement with the numbers 10:20 required by the oxide NiO_2 , the existence of which has been assumed by Dufau (Abstr., 1897, ii, 200). This oxide readily loses oxygen, forming substances which vary in composition with the conditions, and to which no definite formulæ can be given. (5) When nickel dioxide loses oxygen, no arrest occurs at the stage Ni_2O_3 , which may, however, represent a relatively stable compound; on drying over calcium chloride at 100° , it passes always into compounds for which the ratio of Ni:O is in some cases approximately 10:14 and in others 10:13.

Nickel hence behaves differently from cobalt, which forms an oxide, Co_2O_3 , capable of being dried at 100° without decomposing. The oxides, which have been described as Ni_2O_3 and Ni_3O_4 , must be regarded as mixtures of NiO_2 and NiO . T. H. P.

Perchromic Acids. E. H. RIESENFELD [with KUTSCH, OHL, and WOHLERS] (*Ber.*, 1905, 38, 3380—3384. Compare this vol., ii, 461; and Hofmann and Hindlmaier, *ibid.*, 716).—Hydrogen peroxide oxidises alkaline solutions of chromic acid to form reddish-brown salts derived from the acid H_3CrO_8 . If, however, the solution is acidified with almost any acid (hydrochloric, oxalic, or acetic) before the peroxide is added, crystalline, blue salts derived from the acid H_3CrO_7 are formed (compare Wiede, Abstr., 1898, ii, 28, 295). On adding hydrogen peroxide to an aqueous solution of chromic acid containing excess of pyridine, a blue pyridine salt, PyHCrO_5 , derived from the acid HCrO_5 , is obtained. Yellow crystals of the composition $\text{CrO}_4 \cdot 3\text{NH}_3$ are formed when the solution used in preparing the salt $(\text{NH}_4)_3\text{CrO}_8$ (*loc. cit.*) is kept for twenty-four hours.

The salts of the acids named can be converted into one another. On adding an acid to an aqueous suspension of the salt $(\text{NH}_4)_3\text{CrO}_8$, oxygen is evolved and the blue substance $(\text{NH}_4)_2\text{H}_2\text{CrO}_7$ produced. On adding an excess of pyridine to either of these salts, the compound PyHCrO_5 is formed. Finally, from any of the preceding substances the compound $\text{CrO}_4 \cdot 3\text{NH}_3$ is obtained by the action in aqueous solution of an excess of ammonia.

A brief discussion is given of the nature of these substances and the manner of their formation. Names will be given to them only after a more complete investigation has been made. W. A. D.

Decomposition of Chromic Acid by means of Hydrogen Peroxide. E. H. RIESENFELD [with KUTSCH and OHL] (*Ber.*, 1905, 38, 3578—3586. Compare Berthelot, *Abstr.*, 1889, 350, 468, 571; Baumann, *Abstr.*, 1891, 245; Bach, *Abstr.*, 1902, ii, 251).—If hydrogen peroxide is dropped into a mixture of 0.1*N* potassium dichromate solution and 10 per cent. sulphuric acid, the chromic acid being always in excess and the temperature remaining constant at 13.52—18.26°, the amount of oxygen evolved is slightly less (2.89 instead of 3) than that required by the equation $2\text{CrO}_3 + 3\text{H}_2\text{O}_2 = \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{O}_2$, whilst if the chromic acid solution is dropped into the hydrogen peroxide, the latter being always in excess, a blue coloration is formed which gradually disappears, and the volume of oxygen liberated is equivalent to 4.14—4.97; average, 4.51 mols. of oxygen for each mol. of chromic acid. The reaction takes place, therefore, mainly according to the equations: $2\text{H}_2\text{CrO}_4 + 7\text{H}_2\text{O}_2 = 2\text{H}_3\text{CrO}_8 + 6\text{H}_2\text{O}$; $2\text{H}_3\text{CrO}_8 = \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O} + 5\text{O}_2$, the evolution of a slightly less amount of oxygen than required by these equations being due to formation of a small amount of the perchromic acid, H_3CrO_7 . The blue coloration in ethereal solution is formed by the perchromic acids, H_3CrO_8 and H_3CrO_7 , as well as by the anhydride, CrO_4 . The decomposition of perchromic acid, H_3CrO_8 , is not affected by the presence of hydrogen peroxide, as the amount of oxygen evolved is the same if the decomposition takes place in acid solution or in acid solution with addition of a limited amount of 3 per cent. or 30 per cent. hydrogen peroxide.

If in the oxidation of alkaline chromate solutions by means of hydrogen peroxide the solution is allowed to become warm, the perchromate formed does not separate, but decomposes into chromate and oxygen, the oxidation and decomposition taking place successively until the hydrogen peroxide is completely reduced, the chromate acting as a catalytic agent, as observed by Berthelot. G. Y.

Molybdates. ADOLF JUNIUS (*Zeit. anorg. Chem.*, 1905, 46, 428—448).—*Thallium paramolybdate*, $5\text{Tl}_2\text{O} \cdot 12\text{MoO}_3$, is obtained by double decomposition from a hot solution of the sodium salt as a yellow, microcrystalline precipitate very easily soluble in alkali hydroxides and carbonates and in mineral acids. When heated, it becomes dark yellow, at a red heat it melts to a dark brown liquid, and finally decomposes with slight volatilisation.

Barium paramolybdate is obtained by double decomposition as a precipitate which dissolves again in excess of barium chloride. From the solution, a bulky precipitate separates after some time, of the formula $5\text{BaO} \cdot 12\text{MoO}_3 \cdot 20\text{H}_2\text{O}$. When boiling solutions of the molybdate and chloride are employed, a salt with $10\text{H}_2\text{O}$ is obtained.

It was not found possible to prepare lead, cadmium, or silver paramolybdates, the normal salt being obtained in each case.

Electrolysis of sodium, potassium, and ammonium molybdates leads eventually (when a diaphragm is employed) to the production of free molybdic acid; limited electrolytic action gives intermediate products.

Sodium molybdate with a current of 6.7 amperes per sq. cm. at 7 to

10 volts gives, after electrolysis for about an hour, a faintly alkaline anodic solution from which the salt $5\text{Na}_2\text{O}, 12\text{MoO}_3, 36\text{H}_2\text{O}$ may be crystallised. Long-continued electrolysis gives an acid anodic solution from which alcohol deposits crystals of $\text{Na}_2\text{O}, 3\text{MoO}_3$ with 9 or $11\text{H}_2\text{O}$.

Potassium molybdate gives, similarly, the salt $5\text{K}_2\text{O}, 12\text{MoO}_3, 8\text{H}_2\text{O}$ after a short interval, and later $\text{K}_2\text{O}, 3\text{MoO}_3, 2\text{H}_2\text{O}$; potassium trimolybdate, unlike the sodium salt, does not effloresce.

Ammonium molybdate yields, on electrolysis, the paramolybdate or $5(\text{NH}_4)_2\text{O}, 12\text{MoO}_3, 7\text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{O}, 4\text{MoO}_3, 2\frac{1}{2}\text{H}_2\text{O}$ or molybdic acid according to the conditions; the second of these compounds (the tetra- or meta-molybdate) may also be obtained by the addition of hydrochloric acid to a solution of ordinary ammonium molybdate until the liquid reddens methyl-orange, and crystallisation. Similarly, as was confirmed by measurements of the electrical conductivity, sodium paramolybdate may be transformed into the tetra-salt according to the equation $2\text{Na}_{10}\text{Mo}_{12}\text{O}_{41} + 8\text{HCl} = 6\text{Na}_2\text{Mo}_4\text{O}_{13} + 8\text{NaCl} + 4\text{H}_2\text{O}$. Electrolytic reduction of molybdic acid in strong hydrochloric acid solution gives at the cathode a precipitate of the blue oxide, to which the formula Mo_7O_{20} is ascribed instead of the Mo_5O_{14} of Berzelius or the Mo_3O_8 of Muthmann.

D. H. J.

Solid Solutions of Indifferent Gases in Uranium Oxide. II. VOLKMAR KOHLSCHÜTTER and K. VOGDT (*Ber.*, 1905, **38**, 2992—3002. Compare this vol., ii, 394).—In reply to Friedheim (this vol., ii, 530), details are given of quantitative experiments which support the authors' views as to the reaction which takes place when hydroxylamine uranate is heated and the nature of the residue.

G. Y.

Double Carbonate of Uranyl and Ammonium. FEDERICO GIOLITTI and V. VECCHIARELLI (*Gazzetta*, 1905, **35**, ii, 170—181).—On mixing a concentrated solution of ammonium carbonate (5 mols.) with one of uranyl nitrate (2 mols.) at 50 — 55° , the liquid deposits, on cooling, a bright yellow, crystalline mass of the soluble double salt, $2\text{UO}_2\text{CO}_3, 3(\text{NH}_4)_2\text{CO}_3, 4\text{H}_2\text{O}$, which is probably identical with the salt obtained by Plate (Gmelin-Kraut, *Handbuch anorg. Chem.*, 2nd ed., **2**, 411); the addition of alcohol to the mother-liquor causes the deposition of a bright yellow powder, which is soluble in water and in which the ratio of NH_3 :U has the value 9:4.

A solution containing excess of ammonia, together with uranyl nitrate (1 mol.) and ammonium carbonate (3 mols.), deposits the double salt, $\text{UO}_2\text{CO}_3, 2(\text{NH}_4)_2\text{CO}_3$, in the form of yellow crystals, which lose ammonia at the ordinary temperature and more readily on heating, either in the dry state or in solution; the ratio between NH_3 and CO_2 always remains, however, the same, that is, 4:3, so that it must be assumed that the salt splits up completely into the two parts UO_2O and $\text{CO}_2, 2(\text{NH}_4)_2\text{CO}_3$. The formation of complex ions with this double salt is confirmed by cryoscopic measurements, which indicate an increasing and ultimately almost complete electrolytic dissociation.

T. H. P.

Equilibrium Phenomena with the Hydrates of Uranous Sulphate. I. Properties of Uranous Sulphate. FEDERICO GIOLITTI and G. BUCCI (*Gazzetta*, 1905, 35, ii, 151—161).—By the interaction of varying quantities of uranyl sulphate, alcohol, water, and sulphuric acid, the authors have prepared the following hydrates of uranous sulphate: (1) $\text{U}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$, which forms small, dark green crystals and, when treated with a large quantity of cold water, is mostly dissolved, whilst about 25 per cent. of it is converted into a green, powdery basic salt, $\text{UOSO}_4 \cdot 2\text{H}_2\text{O}$; the extent of the hydrolysis effected by water depends on the temperature. If the salt is acted on by a small proportion of water, the basic salt at first separated gradually dissolves and a solution of the normal sulphate is obtained. Ten per cent. sulphuric acid solution dissolves the octahydrate without hydrolysing it. When heated in absence of air, it passes into the tetrahydrate at about 90° , into the anhydrous salt at about 300° , and when ignited, firstly into UO_2SO_4 , and finally into U_3O_8 . Graphic representation of the rate of loss of water by the octahydrate when kept in a desiccator over sulphuric acid indicates the existence of the hydrates: $\text{U}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$, $\text{U}(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$, and $\text{U}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. (2) The tetrahydrate, $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, which behaves similarly to the octahydrate on heating and is more readily decomposed than the latter by water. T. H. P.

Equilibrium Phenomena with the Hydrates of Uranous Sulphate. II. Octahydrate and Tetrahydrate of Uranous Sulphate. FEDERICO GIOLITTI and G. BUCCI (*Gazzetta*, 1905, 35, ii, 162—169. Compare preceding abstract).—Microscopical study of the transformation of the octa- into the tetra-hydrate of uranous sulphate shows that this change proceeds at 68 — 87° , and hence takes place where the octahydrated sulphate is in a condition of metastable equilibrium. Solutions of the octahydrate are relatively very stable between 18° and 105° , so that the separation of the tetrahydrate sometimes occurs only with difficulty; the exact temperature at which the conversion into the lower hydrate takes place has not been determined. A saturated solution of the unchanged octahydrate contains, at 18° , 10·17 per cent., and at 93° , 63·2 per cent. of $\text{U}(\text{SO}_4)_2$, whilst that of the tetrahydrate contains, at 24° , 9·8 per cent., at 37° , 8·3 per cent., at $48\cdot2^\circ$, 8·1 per cent., and at 63° , 8·3 per cent. of $\text{U}(\text{SO}_4)_2$. The results obtained show that, at temperatures below 18 — 20° , the octahydrate, which, since it has a less solubility than the tetrahydrate, is the stable form in which uranous sulphate crystallises, is labile at any higher temperatures, the stable form then being the tetrahydrate. The pale green powder obtained by the interaction of 42 grams of uranyl sulphate, 168 grams of water, 336 grams of alcohol, and 41 grams of sulphuric acid under the influence of sunlight, has the composition $\text{U}(\text{SO}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. T. H. P.

Zirconiumsulphuric Acids. RUDOLF RUER and MAX LEVIN (*Zeit. anorg. Chem.*, 1905, 46, 449—455).—It has already been shown (this vol., ii, 41) that zirconium sulphate is more correctly considered as zirconiumsulphuric acid. It now appears that there exists another, probably a series of these zirconiumsulphuric acids containing more

zirconium than the normal sulphate and yielding on electrolytic dissociation complex anions containing both zirconium and the sulphate group. The so-called basic zirconium sulphate obtained by dissolving zirconium hydroxide in a solution of neutral zirconium sulphate at 100°, seems in reality to be a solution of zirconiumsulphuric acids, to which the formula $(\text{ZrO}_2)_n(\text{SO}_3)_m(\text{H}_2\text{O})_p$, where $n > m/2$, must be assigned.

The tendency of zirconium to form zirconiumsulphuric acids, richer in metal than the normal salt, explains the difference which a solution of normal zirconium sulphate shows, according to whether it has been prepared in the cold or by boiling; in the heated solution there is formed a zirconiumsulphuric acid, and free sulphuric acid; the latter, as proved experimentally, increasing the electrical conductivity.

D. H. J.

Bismuth Telluride. K. MÖNKEMEYER (*Zeit. anorg. Chem.*, 1905, 46, 415—422).—A fusion diagram for bismuth and tellurium has been constructed by Tammann's method, and it has thus been found that there is only one definite compound formed, namely, Bi_2Te_3 . The curve of fusion shows a maximum point (corresponding with the compound mentioned) at 573° and 52.14 per cent. of bismuth, and two eutectic points at 261° and 99.08 per cent. of bismuth and at 388° and 13.91 per cent. of bismuth respectively.

D. H. J.

Columbium and Tantalum. EDGAR F. SMITH [with ROY D. HALL, MARY E. PENNINGTON, and C. W. BALKE] (*Chem. Centr.*, 1905, ii, 1160—1161; from *Proc. Amer. Phil. Soc.*, 44, 151—158. Compare *Abstr.*, 1904, ii, 824).—Although Marignac found titanium in columbium, the oxide of the latter prepared from potassium columbofluoride has not been found to give the characteristic tests for titanium with hydrogen peroxide and chromotropic acid. Attempts to separate titanium chloride from the crystalline chloride, prepared by means of sulphur monochloride, also failed. Potassium tantalofluoride has been isolated under conditions which precluded the possibility of the presence of the titanium double fluoride and double fluorides of tantalum with caesium, $\text{TaF}_5\cdot\text{CsF}$ and $\text{TaF}_5\cdot 2\text{CsF}$, ammonium, $\text{TaF}_5\cdot 2\text{NH}_4\text{F}$ and $\text{TaF}_5\cdot 3\text{NH}_4\text{F}$, rubidium, $2\text{TaF}_5\cdot\text{RbF}$, potassium, $\text{TaF}_5\cdot 2\text{KF}$, and sodium, $\text{TaF}_5\cdot 2\text{NaF}$ and $\text{TaF}_5\cdot 3\text{NaF}$, have been obtained. Marignac's atomic weight determinations were very possibly rendered inaccurate by the presence of one of these ammonium compounds in the double fluorides of potassium and ammonium which he employed; moreover, the substance which he regarded as potassium titanofluoride has been found in the columbium and not in the tantalum fraction, and is not sparingly soluble. Attempts to separate this substance, however, by fractional precipitation with aqueous solutions of ammonia, fractional crystallisation of the double fluorides, fractional chlorination of the oxides in presence of carbon, or by the action of numerous organic bases, have failed.

Hermann's statement that the acid mother liquor obtained by repeatedly crystallising potassium columboxyfluoride from water and dilute hydrofluoric acid yields a slimy substance which, when treated with sodium ammonium hydrogen phosphate before the blow-

pipe, forms a yellow mass, has been confirmed, but this substance, which was supposed to be sodium neptunate, has been found to consist of a mixture of tantalum and iron together with some columbium. The removal of tungsten and tin from the oxides of columbium and tantalum can be effected with slight loss by repeated fusion with sodium carbonate and sulphur, but not by the ammonium sulphide method. Complex compounds of tantalum and columbium oxides with tungstic acid have also been prepared.

E. W. W.

Columbium. ROY D. HALL and EDGAR F. SMITH (*Chem. Centr.*, 1905, ii, 1161—1163; from *Proc. Amer. Phil. Soc.*, 44, 177—212).—A sample of columbite from Lawrence County, South Dakota, had a sp. gr. 5.86 and contained 81 per cent. of the oxides of columbium and tantalum; iron, manganese, zinc, uranium, copper (?), and nickel (?), together with acids of tantalum, columbium, titanium, lithium, zirconium, tin, and tungsten, were also present. The mother liquors of the potassium tantalofluoride obtained in the method of treatment employed yielded hard, hexagonal crystals of potassium columbofluoride, K_2CbF_7 , and by evaporating the former with sulphuric acid and precipitating with potassium hydroxide, potassium tantaloxyluoride was obtained. Potassium columboxyluoride, $K_2CbOF_5 \cdot H_2O$, from which the tantalum had been removed by means of sulphuric acid, was soluble. The oxide formed by the ignition of the columbium double fluoride, when tested by the colorimetric method, was found to contain 0.18 per cent. of titanium oxide.

The following methods were employed for the separation of titanium oxide from columbium oxide. (1) Crystallisation of potassium columbofluoride; this method failed to effect a separation, since the presence of hydrofluoric acid increased the solubility of the columbium and decreased that of the titanium compound. (2) Fractional precipitation with ammonia; columbium hydroxide is first precipitated, but no fraction was found to consist entirely of titanium hydroxide, and the last contained a considerable quantity of columbium. (3) Preparation of the chlorides and oxychlorides of columbium and the chloride of tantalum and separation of the latter by distillation. (4) Treatment of the hydroxides with rather concentrated cold sulphuric acid; titanium hydroxide is soluble, but columbium hydroxide is not. (5) Action of various bases on the double fluorides. Whilst an excess of sodium hydroxide gives a precipitate with a solution of potassium titanofluoride which is insoluble in water, the precipitate formed by sodium or potassium hydroxide in a solution of potassium columboxyluoride dissolves in a slight excess of the alkali, but separates out again in a crystalline form when a large excess is added; when both metals are present, however, the precipitate also contains both. Potassium hydroxide gives a heavy precipitate with solutions of potassium titanofluoride.

Experiments on the action of seventy-four bases in solutions of potassium titanofluoride and potassium columboxyluoride gave the following results. A portion of the bases completely precipitated titanium but not columbium, the latter being soluble in excess and forming a columbate. Columbium was found in the precipitate, how-

ever, and titanium in the solution, the latter being present possibly in the form of a complex titanocolumbic acid (?). The hydroxides of both metals were precipitated by another portion of the bases, which included quinoline, but titanium hydroxide was only partially soluble in excess of the base. A third portion did not precipitate titanium; columbium was partially precipitated, but carried down some titanium. Other bases did not give precipitates with either metal.

The action of solutions of the double fluorides of columbium, titanium, tantalum, tin, and tungsten in sulphuric acid on codeine, morphine, resorcinol, naphthol, pyrogallol, salicylic acid, cinchonidine, *apomorphine*, *narceine*, *berberine*, and *narcotine* has been examined. Solutions of tin gave no colour reactions. The colorations in other cases were destroyed by dilution, *narceine* and *berberine* being the only alkaloids which gave distinctive colorations. The morphine test for titanium proved trustworthy, but even in this case the presence of less than 0.5 per cent. of titanium oxide in columbium oxide could not be detected. Codeine gave no reaction with columbium and resorcinol, but a slight coloration with tantalum, columbium, or tungsten; the latter, however, afforded a trustworthy test for titanium.

Calcined columbium oxide volatilises in a stream of dry hydrogen chloride, forming a white powder which is insoluble in oxalic acid, but dissolves slowly in boiling sulphuric acid; it has probably the composition $\text{Cb}_2\text{O}_5, x\text{HCl}$.

If ammonia is added to solutions of the double fluorides of columbium and titanium and the precipitated hydroxides allowed to remain with a solution of sulphuric acid of sp. gr. 1.145, the titanium precipitate is completely dissolved, whilst the columbium is not attacked; when a mixture of the solutions is used, however, the solution and residue contain both metals.

In estimating titanium by means of chromotropic acid, the presence of free mineral acids should be avoided; the method is not in any way superior to the hydrogen peroxide method.

By the action of carbon tetrachloride on calcined titanium oxide at a red heat, it is slowly but completely converted into the chloride, whilst columbium oxide rapidly forms the oxychloride at a lower temperature. The chloride is quickly formed by heating at 200—225° or by subliming the oxychloride in carbon tetrachloride vapour; calcined tantalum oxide is also rapidly converted into the chloride (compare Delafontaine and Linebarger, *Abstr.*, 1896, ii, 653). If the carbon tetrachloride contains traces of moisture, oxychloride is formed and dissolved in the chloride; on sublimation, the oxychloride remains in the form of a glassy residue. Columbium oxychloride sublimes in closed tubes, forming lustrous, silky needles; the chloride CbCl_5 which is obstinately retained by the oxychloride, is best removed by subliming in a stream of chlorine over columbium oxide; when carbon tetrachloride is present, columbium chloride is also formed.

Columbium chloride, prepared by the action of sulphur monochloride on the oxide or by heating the oxide with carbon tetrachloride, forms large, yellow, needle-like crystals; it is readily soluble in carbon tetrachloride or sulphur monochloride, forming yellow and red solutions respectively. When the yellow ethereal solution is evaporated on

the water-bath, a viscid liquid is left and acid fumes are evolved; on calcination, the oxide is formed. By the action of gaseous ammonia on the ethereal solution, ammonium chloride and columbium nitride are formed. The chloride is soluble in chloroform, but on heating the solution a brown powder is formed. When the alcoholic solution of the chloride is warmed and concentrated, vapours are given off which are possibly caused by the formation of ethyl columbate. Aniline and pyridine form additive compounds. Solutions in carbon tetrachloride, which is the best solvent, may be used for the preparation of double chlorides.

Potassium oxyfluoropercolumbate, $\text{KCbO}_2\text{F}_5 \cdot \text{H}_2\text{O}$, prepared by the action of a 3 per cent. solution of hydrogen peroxide on potassium columboxyfluoride, forms pale yellow crystals; the colour of the solution in water containing a small quantity of hydrogen peroxide is more intense, and on addition of potassium titanofluoride becomes of a still deeper shade, but it is destroyed by the addition of hydrofluoric acid. Acid molybdenum solutions give a similar coloration, but a quantitative colorimetric estimation showed that columbium was not present. The yellow colour of solutions of columbium in hydrofluoric acid cannot be ascribed to the presence of titanium, which gives a straw-yellow coloration, but is probably caused by the greenish-yellow colour of the columbium itself. The yellow hydroxide, $\text{Cb}(\text{OH})_6$ or $\text{Cb}_2\text{O}_5 \cdot \text{H}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$, is prepared by treating the double fluoride with sulphuric acid, expelling the excess of acid, extracting with water, and adding hydrochloric acid and hydrogen peroxide; it loses water and oxygen on calcination and becomes white. The colour of the higher oxides appears to be characteristic of columbium, and not to be due to the presence of titanium. The solubility of potassium titanofluoride is increased by the addition of hydrogen peroxide, whilst that of the corresponding columbium compound is decreased; the presence of hydrofluoric acid has the reverse effect.

Tin and tungsten may probably be separated from potassium columbofluoride by crystallisation from hydrofluoric acid. The presence of tin was shown by the stains formed in the platinum crucible when the partially dried oxide was ignited. If disodium hydrogen phosphate is added to a solution which contains a large excess of columbium and a small quantity of titanium, no precipitate is formed, but on increasing the quantity both metals are completely precipitated. Geisow's observation that titanium and zirconium can be separated from columbium by means of an alkaline solution of formoxime has not been confirmed. Tantalum is only incompletely precipitated. Potassium iodate, which does not contain periodate, does not form precipitates with columbium or titanium, but both metals are precipitated from acid solutions.

E. W. W.

Columbates. M. HUME BEDFORD (*J. Amer. Chem. Soc.*, 1905, 27, 1216—1221).—The following sodium columbates have been described by Rose: $\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ (or $9\text{H}_2\text{O}$); $3\text{Na}_2\text{O} \cdot 2\text{Cb}_2\text{O}_5 \cdot 24\text{H}_2\text{O}$; $3\text{Na}_2\text{O} \cdot \text{Cb}_2\text{O}_5$; and $4\text{Na}_2\text{O} \cdot 5\text{Cb}_2\text{O}_5$. A fifth salt, $3\text{Na}_2\text{O} \cdot 4\text{Cb}_2\text{O}_5 \cdot 21\text{H}_2\text{O}$, has been obtained by Hermann. It is now shown that the methods employed by these authors yield only one sodium columbate, and that

this has the formula $7\text{Na}_2\text{O}, 6\text{Cb}_2\text{O}_5, 32\text{H}_2\text{O}$. This salt is very stable, and crystallises well from aqueous solutions. The corresponding *barium* salt, $7\text{BaO}, 6\text{Cb}_2\text{O}_5, 18\text{H}_2\text{O}$, the *silver* salt, $7\text{Ag}_2\text{O}, 6\text{Cb}_2\text{O}_5, 5\text{H}_2\text{O}$, and the *zinc* salt, $7\text{ZnO}, 6\text{Cb}_2\text{O}_5, 25\text{H}_2\text{O}$, are described.

The following method is recommended for the separation of columbic and tungstic acids. The solution containing these acids is treated with a solution of mercurous nitrate and a slight excess of nitric acid. Freshly-precipitated mercuric oxide is added, and the mixture is boiled for five minutes. The precipitate is collected, washed, dried, ignited, and weighed. The mixture of the two oxides thus obtained is fused with potassium carbonate, and the product is dissolved in water. An excess of magnesia mixture is added to the solution, and the precipitate produced is left for several hours and then collected, washed five or six times with magnesia mixture, dried, and ignited. The residue is fused with potassium hydrogen sulphate, and the product is boiled with water, filtered, washed, ignited, and the columbic oxide is weighed. The amount of tungstic oxide present in the mixture is obtained by difference.

E. G.

[Platinum Compounds.] ITALO BELLUCCI (*Gazzetta*, 1905, 35, ii, 334—340. Compare Blondel, this vol., ii, 720).—The author dissents from Blondel's deductions (*loc. cit.*), as these he considers are based on purely hypothetical foundations, and are in disaccord with the author's experimental results (compare Bellucci and Parravano, this vol., ii, 395).

T. H. P.

Chemical Properties and Combining Weight of Palladium.

RICHARD AMBERG (*Annalen*, 1905, 341, 235—308).—An historical summary of the methods which have been used for quantitative precipitation of palladium and a *résumé* of the different attempts which have been made to determine its atomic weight are given in the introduction.

In the search for suitable compounds of palladium for atomic weight determinations, a number of new additive derivatives with amine bases have been prepared and studied. The *compounds* with aniline, α - and β -naphthylamines, diphenylamine, dibenzylamine, *m*-phenylenediamine, benzidine, phenylhydrazine, pyridine, quinoline, acridine, tribenzylamine, and triamylamine, are described in tabular form. None of them proved suitable for atomic weight determinations, and palladosoammine chloride was finally chosen for this purpose. The salt was prepared in various ways from a specimen of pure palladium (prepared by Siebert).

A number of experiments was made in order to ascertain the most satisfactory method of estimating the palladium in this salt. Finally, the electrical deposition of the palladium was effected in a solution of the salt in dilute sulphuric acid, the operation being carried out in a Classen platinum dish. In the first series of experiments (5 determinations), the chlorine was estimated, the salt being first electrolysed in dilute ammoniacal solution or in acid solution, but the latter was preferred. From the solution freed from precipitated palladium by filtration, the chlorine was precipitated

as silver chloride. In the second series (6 experiments), the chlorine was estimated after precipitation of the palladium with hydrazine sulphate. In the third series (12 experiments), the metal was estimated in solutions containing from 1 to 16 per cent. of sulphuric acid; the electrode was rapidly rotated (from 600—1000 rotations per minute), and the temperature maintained at 60—65°; the current varied from 0.05 to 0.4 ampere, and the voltage was kept below 1.25 volts. The current was maintained whilst the contents of the dish cooled. The palladium was finally collected and dried at 110°. The relation between the precipitation of the metal and the rapidity of rotation of the electrode is discussed. The rapidity of precipitation at the current strength and concentration here used is dependent on the rapidity of stirring, the temperature, and the diffusion-coefficient.

The greatest stress is laid on the direct estimation of the metal by the method just described. The atomic weight of palladium is given as 106.688 ± 0.006 ($O = 16$). This extremely high value is not in accord with the differences seen in the series of the periodic system, thus: $Ru = 101.7$, $Rh = 103.0$, $Pd = 106.7$, $Ag = 107.93$. The old value of the atomic weight of palladium (105.2) shows the differences which would be expected. It is, however, thought, when allowance is made for various possible errors, that the atomic weight is approximately 106.7.

K. J. P. O.

Mineralogical Chemistry.

Hydrocarbons in Louisiana Petroleum. II. CHARLES E. COATES and ALFRED BEST (*J. Amer. Chem. Soc.*, 1905, 27, 1317—1321. Compare Abstr., 1904, ii, 45).—Three further samples of Louisiana petroleum have been examined, but of these only one, which was obtained from Bayou Bouillon, near St. Martinsville, was in sufficient quantity for extended investigation. The results of the examination of this specimen showed that the oil was composed mainly of hydrocarbons of the series C_nH_{2n-2} , and C_nH_{2n-4} , and no evidence was obtained of the presence of unsaturated compounds or of optical activity. E. G.

Thorianite, a New Mineral from Ceylon. WYNDHAM R. DUNSTAN and GEORGE S. BLAKE (*Proc. Roy. Soc.*, 1905, A, 76, 253—265. Compare Dunstan, Abstr., 1904, ii, 744).—The crystallographic character of thorianite is described, and the results of analysis of another specimen of the mineral are communicated. The percentages of the various constituents are given as follows:

ThO ₂ .	UO ₂ .	UO ₃ .	CeO ₂ , La ₂ O ₃ and Di ₂ O ₃ .	PbO.	Fe ₂ O ₃ .	CaO.	He.	P ₂ O ₅ .	Insoluble in nitric acid.
78·86	6·03	9·07	1·02	2·59	0·46	1·13	0·39	trace	0·20

Thorianite possesses the advantage, not shared by any known thorium mineral, of containing uncombined thoria, soluble in nitric acid with formation of thorium nitrate. The powdered mineral dissolves readily also in diluted sulphuric acid with evolution of a gas which is chiefly helium. Thorianite is scarcely attacked by hydrochloric acid. The hardness of thorianite is nearly 7, and the density of different specimens varies from 8—9·7.

So far as the investigation has gone it appears probable that thorianite is isomorphous with uraninite, and that in the thorianite of Ceylon some of the thoria is replaced by the corresponding uranium oxide. The evidence, however, is not sufficient to show whether this is a case of isomorphous mixture, as seems probable, or of true chemical replacement.

Thorianite is highly radioactive, and measurements of the rate of decay of the emanation indicate the presence of radium in the mineral (compare also Hahn, this vol., ii, 432, 789). J. C. P.

Crystallised Slag from Hettstedt: Composition of Melilite. FERRUCCIO ZAMBONINI (*Zeit. Kryst. Min.*, 1905, 41, 226—234).—Large, cube-shaped crystals, measuring 16×19 mm., in a blast-furnace slag from the Seigerhütte at Hettstedt, near Mansfeld, in Prussian Saxony, have been analysed (anal. I) by W. STAHL (*Berg- und Hüttenm. Zeit.*, 1904, 63, 273—274); he described the crystalline form as cubic, and was unable to identify the material. A new examination proves the crystals to be melilite and of the form common in slags. The double refraction is very feeble and negative in sign, but portions of some crystals are isotropic; pleochroism is distinct. The crystals enclose numerous impurities. A redetermination of the silica gave 37·69 per cent.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.†	35·80	9·34	—	21·50	—	24·50	2·74	0·85	1·36	—	100·71
II.	40·14	6·47	9·95	0·53	trace	32·98	6·33	1·49	2·18	0·27	100·34
III.	39·20	7·56	11·34	trace	trace	32·18	6·41	1·45	2·21	0·21	100·56

† Also: ZnO, 4·00; NiO, 0·19; (Cu₂,Ni)S, 0·43; Pb, As, traces. Sp. gr. 3·05.

New analyses are given of the natural melilite of Capo di Bove, near Rome; II, of yellow crystals, and III, of brown crystals.

From Damour's analyses of natural melilite, Des Cloizeaux deduced the formula $12R'O, 2R_2O_3, 9SiO_2$, which was written by Rammelsberg as $Na_2(Ca, Mg)_{11}(Al, Fe)_4Si_9O_{36}$, whilst Groth deduced $(Ca, Mg)_6(Al, Fe)_2Si_5O_{19}$.

Vogt has attempted to explain the composition by isomorphous mixtures of gehlenite, $R_3''R_2'''Si_2O_{10}$, and äkermanite, $R_4''Si_3O_{10}$, but this is not supported by the analyses. According to Vernadsky's theory of the silicates (*Abstr.*, 1901, ii, 249), the formula may be written as $R''R_2'''Si_2O_8, nR_2''SiO_4$; Des Cloizeaux's formula will then be $2R''R_2'''Si_2O_8, 5R_2''SiO_4$. L. J. S.

Physiological Chemistry.

Action of Oxygen on the Sickness produced by Rarefaction of the Air. Experiments on an Orang-Outang. ALBERTO AGGAZZOTTI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 94—103 and 180—187).—The symptoms observed on the respiration of air at great altitudes are not due alone to the diminished partial pressure of the oxygen. Air rich in oxygen has a beneficial action on the sickness produced by barometric depression, and up to a certain point this beneficial action is proportional to the percentage of oxygen in the inspired air; but with very great rarefactions, the symptoms are observed, whatever the content of oxygen in the air (compare Mosso, *Abstr.*, 1904, ii, 577 and 622). If the amount of carbon dioxide in the inspired air is increased to a certain value, more considerable dilution of the air can be withstood without injurious effects, and the greater the proportion of carbon dioxide the more can the air be diluted. Carbon dioxide does not exert this beneficial action unless its partial pressure in the air exceeds 18 mm. T. H. P.

Simultaneous Action of Oxygen and Carbon Dioxide on the Sickness produced by Rarefaction of the Air. Experiments on an Orang-Outang. ALBERTO AGGAZZOTTI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 256—264. Compare *Abstr.*, 1904, ii, 746, and preceding abstract).—Only air which is rich in both carbon dioxide and oxygen can alleviate the ill-effects which are produced by lowering of the barometric pressure. T. H. P.

Experiments on a Man breathing Carbon Dioxide and Oxygen together under a Barometric Pressure of 122 mm., corresponding with an Altitude of 14,582 Metres. ALBERTO AGGAZZOTTI (*Atti R. Accad. Lincei*, 1905, [v], 14, ii, 290—297. Compare preceding abstracts).—The results obtained with the orang-outang are confirmed by those given by similar experiments with a man. At a height of 14,500 metres, man suffers no discomfort if the air breathed contains 13 per cent. of carbon dioxide and 67 per cent. of oxygen. T. H. P.

Restorers of the Cardiac Rhythm. DAVID J. LINGLE (*Amer. J. Physiol.*, 1905, 14, 433—451).—The conclusion is drawn from experiments on heart-strips that certain agents such as the constant current, induction shocks, and mechanical tension, which have been considered capable of producing rhythmical activity, owe their power to the solution of sodium chloride used with them, which, therefore, cannot be looked on as an indifferent fluid. W. D. H.

Electric Conductivity of Blood during Coagulation. ROBERT T. FRANK (*Amer. J. Physiol.*, 1905, 14, 466—468).—No appreciable change occurs in the conductivity of the blood during the coagulation

process. Whether the amount of fibrinogen in the blood is too small to show tangible changes, or whether the numerous chemical and physical changes occurring in the complex process of coagulation exactly neutralise each other could not be determined. The latter explanation appears to be unlikely.

W. D. H.

Osmotic Pressure of Blood and Urine in Fishes. M. C. DEKHUYZEN (*Chem. Centr.*, 1905, ii, 1035—1036; from *Arch. Néerland*, [ii], 10, 121—136).—Certain fish, such as the salmon and eel, are able to pass without inconvenience from the sea, where the pressure is great, into fresh water, where the pressure is much lower. Estimation of the freezing points of blood and urine shows that, by the regulating action of the kidneys, fishes, like warm-blooded animals, are able to maintain the osmotic pressure of their blood at a constant level. The osmotic pressure of the blood of warm-blooded animals varies from 6.75 to 7.25 atmospheres, that of different fresh water cold-blooded animals is about 6 atmospheres, that of marine fishes 8.7 atmospheres.

W. D. H.

Effect of Intravenous Injections of Bile on Blood-pressure. S. J. MELTZER and WILLIAM SALANT (*J. exper. Med. New York*, 1905, 7, 280—291).—Although, as previous observers have shown, the influence of bile salts on blood-pressure is slight, that of the entire bile is very marked, leading to a great depression of the arterial pressure. The rate of injection makes a considerable difference, rapid injection producing the most marked, or even fatal results. The effect, like that of potassium salts, is mainly cardiac. In some experiments, intravascular coagulation was noticed.

W. D. H.

Action of Potassium Salts on the Circulatory Organs. P. TETEUS HALD (*Chem. Centr.*, 1905, ii, 1107; from *Arch. exp. Path. Pharm.*, 53, 227—260).—In rabbits, injection of hypertonic solutions of potassium chloride produces a slow pulse and fall of arterial pressure; sometimes slow but high elevations of the pulse occur. If the dose is not large enough to be immediately fatal, the salt gets into the tissues, and, after about half an hour begins to be eliminated by the kidneys; thus the poison is removed from the body.

W. D. H.

Resistance of the Corpuscles of Fœtal Blood. ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1905, ii, 1035; from *Ann. Soc. Med. Gand*, 85, 152).—Hamburger has pointed out that the corpuscles of fœtal blood are more resistant to saline solutions than are those of the mother. The amount of resistance to 20 per cent. alcohol, amyl alcohol, and absinthe (hæmolytic agents) is about 5 per cent. greater than that of the maternal blood corpuscles.

W. D. H.

Influence of Concentration of Blood-corpuscles and the Form of the Reagent Vessel on Hæmolysis by Chemical Reagents. ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1905, ii, 1035; from *Ann. Soc. Med. Gand*, 1905, May).—The rapidity of hæmolysis

increases with the diameter of the vessel employed. The number of blood-corpuscles in narrow tubes has only a small influence on the rapidity of the hæmolytic reaction. W. D. H.

The Proteids of the Blood. P. MORAWITZ (*Beitr. chem. Physiol. Path.*, 1905, 7, 153—164).—Some recent researches appear to indicate that the albumin of the blood is in closer relationship to the proteid in the food than the globulin, which some believe is formed at the expense of the albumin. In the present experiments, it is shown that after extensive loss of blood the organism has the power of again forming new proteid matter for the blood, even during hunger, and that the reappearance of the globulin is more rapid than that of the albumin; the latter is probably retained by the organism outside the circulatory system, and during inanition re-enters the blood stream. W. D. H.

Behaviour of Salt Solutions in the Stomach. THEODORE PFEIFFER (*Chem. Centr.*, 1905, ii, 1108—1109; from *Arch. exp. Path. Pharm.*, 53, 261—279).—Solutions of sodium sulphate were introduced into the stomachs of dogs with an œsophageal fistula, so that no saliva entered the stomach. After a time, the solution was withdrawn and its freezing point determined. It was found that the stomach wall does not absorb the salt from either hypertonic or hypotonic solutions, but often water passes into the stomach. The exchange of salt between blood and stomach contents is due to simple diffusion. W. D. H.

Examination of Gastric Contents. WILLIAM H. WILLCOX (*Trans. Path. Soc. London*, 1905, 56, 250—259).—A description of methods best available for clinical use in dealing with the gastric contents. The principal tests given are those for the hydrochloric acid and organic acids if present, both qualitative and quantitative. Gunzberg's and the dimethylaminoazobenzene reactions are the best for the detection of the former acid.

In gastric and duodenal ulcer, the acidity is usually high, but organic acids are absent. In temporary dyspepsia, nothing noteworthy was found. In malignant growths of the cardiac portion of the stomach, the total acidity is small, often nil; free hydrochloric acid is always absent. In similar growths of the pyloric portion, the acidity is reduced to half the normal, free hydrochloric acid is scarcely ever present, and organic acids are abundant. W. D. H.

Digestion in Dogs with Artificial Anus. GEORG MAETZKE (*Inaug. Dissert. Breslau Univ.*, 1905, 1—59).—In dogs with a fistula in the ileum, the outflow from the orifice commences within an hour after feeding, or, if much food is given, within half an hour. Foreign particles (pieces of cork) cause delay. The reaction of the contents of the small intestine to phenolphthalein and turmeric is usually acid, but after flesh feeding alkaline. The reaction to lacmoid and methyl-orange is alkaline, except possibly in the upper part of the duodenum. The variations noted in different regions depend on the

amount and character of the food. Trypsin, diastase and invertase are found in varying quantities in the ileum. Leucine and tyrosine are not found even after large quantities of proteid food. If the food given is not excessive, the absorption of proteid, sucrose, and starch is very complete in the small intestine. W. D. H.

The Relationship of the Peptic Digestion Products of Plasteins to Liver Muscles and Other Organs. II. JOSEPH GROSSMANN (*Beitr. chem. Physiol. Path.*, 1905, 7, 165—174).—Experiments are recorded that show that solutions of plastein-albumoses are not only changed into coagulable proteids by the mucous membrane of the alimentary tract, but also by other organs, such as the liver, large intestine, muscles, and brain. W. D. H.

Gastric Digestion of Proteids. HANS LEO (*Zeit. physiol. Chem.*, 1905, 46, 286—292).—Experiments with fibrin tend to show that, to adopt Ehrlich's nomenclature, pepsin plays the part of a thermolabile amboceptor, and hydrochloric acid that of a thermostable complement in gastric digestion. W. D. H.

Pancreatic Secretion. H. G. CHAPMAN (*Proc. Linn. Soc. N. S. Wales*, 1905, 92—100).—Secretin obtained from the echidna, wallaby, Australian water tortoise, and ibis causes a flow of pancreatic juice in the dog, but apparently not in the echidna. The flow produced by pilocarpine is, and that produced by secretin is not, inhibited by atropine. Stimulation of the vagus does not inhibit secretion due to secretin. The pressure of the fluid in the pancreatic duct is equivalent to nine inches of the juice. Pancreatic juice, so far as its proteolytic property is concerned, can be activated by leucocytes. W. D. H.

Action of Pancreatic Juice on Edestin from Cotton Seeds. EMIL ABDERHALDEN and BÉLA REINBOLD (*Zeit. physiol. Chem.*, 1905, 46, 159—175).—The various crystalline products obtained after the digestion of edestin (from cotton seeds) were separated and identified in the usual way. The opinion is supported that the object of digestion is to break down a "foreign proteid" into simple cleavage products, and that this is essential to enable an animal to synthesise the proteids specific to itself. W. D. H.

Chemistry of Digestion in Animals. II. Digestion of Proteids in the Alimentary Tract. E. S. LONDON and A. TH. SULIMA (*Zeit. physiol. Chem.*, 1905, 46, 209—235).—Fistulæ were made in various positions of the alimentary tract in dogs, and proteids of different kinds given as food. The examination of the contents of the canal in different situations and at different intervals after digestion (for albumoses, peptones, crystalline cleavage products, &c.) allows conclusions to be drawn regarding the site and time relationships of digestion and absorption in different parts of the gastro-intestinal tract. W. D. H.

Proteid-katabolism. OTTO COHNHEIM (*Zeit. physiol. Chem.*, 1905, 46, 9—16).—The experiments were made on a dog with a Pawloff's gastric fistula. For several days the animal was given nothing but salt and water; on some days it underwent the process of "sham feeding," which Pawloff has shown causes an abundant flow of gastric juice. But the activity of the digestive organs in itself has no influence on the amount of urinary nitrogen. W. D. H.

Cage for Metabolism Experiments. WILLIAM J. GIES (*Amer. J. Physiol.*, 1905, 14, 403—410).—An illustrated description of an animal cage with various devices for collecting excreta, &c., during metabolism experiments. W. D. H.

Behaviour of Glycyl-*l*-tyrosine in the Dog's Organism after Subcutaneous Injection. EMIL ABDERHALDEN and PETER RONA (*Zeit. physiol. Chem.*, 1905, 46, 176—178).—Certain polypeptides are easily resolved by, whilst others resist, the action of pancreatic juice. It was, therefore, interesting to know what happens to them when introduced parenterally, that is, without the intervention of the digestive juices, for instance, by subcutaneous administration. Accordingly glycyl-*l*-tyrosine was prepared by Fischer's method; this is a dipeptide which is easily resolved by trypsin. It is also completely split up after subcutaneous injection, both glycine and tyrosine being noticeable in the urine. W. D. H.

Behaviour of Cystine, Dialanycystine, and Dileucylcystine in the Organism of the Dog. EMIL ABDERHALDEN and FRANZ SAMUELY (*Zeit. physiol. Chem.*, 1905, 46, 187—192).—The cystine peptides are easily split up by pancreatic juice; the two mentioned were prepared by Fischer's method and their behaviour compared with that of cystine from horse-hair. The administration was in some cases with the food, in others by subcutaneous injection. By either method, cystine increases the amount of oxidised and neutral sulphur in the urine; the dipeptides behave in exactly the same way. The increased amount of sulphur practically accounts for all the cystine given either alone or in combination. The racemic peptides (leucyl-leucine, leucylglycine, &c.) are similarly broken up. W. D. H.

Metabolism of Arginine. WILLIAM H. THOMPSON (*J. Physiol.*, 1905, 33, 106—124. Compare this vol., ii, 268).—If dogs are fed on arginine, the proportion of its nitrogen which reappears as urea varies from 37 to 77 per cent. Part of this is excreted at once, part more slowly, the latter being probably formed by deamidation of the ornithine moiety, and subsequent synthesis of the ammonia into urea. If the arginine is given subcutaneously, the yield of urea-nitrogen is larger. The effects cannot be explained as the result of the solvent (0.9 per cent. sodium chloride) used. The amount of nitrogen excreted as ammonia varies, but averages 10 per cent. of the arginine-nitrogen given. Ornithine, putrescine, or arginine do not appear as such in urine or faeces. In some experiments, a large deficit of nitrogen (37 to 59 per cent.) is accounted for by retention in the body as protoplasm. W. D. H.

Metabolism (Albuminous and Saline) in Man. GEORG VON WENDT (*Chem. Centr.*, 1905, ii, 1109; from *Skand. Arch. Physiol.*, 17, 211—289).—Among the many points raised in this paper are the following: the excretion of sulphur is a better measure of proteid katabolism than that of nitrogen; exogenous is distinguished from endogenous metabolism in relation to purine bases, sulphur, and other substances. The relative constancy of endogenous metabolism is established; the sparing action of non-nitrogenous foods is illustrated; the existence of an "internal circulation" in cell metabolism is suggested.

W. D. H.

Assimilation of Nitrogen, Phosphorus, Calcium, and Magnesium in Man. E. GUMPERT (*Chem. Centr.*, 1905, ii, 1036; from *Med. Klinik.*, 1, 1037—1041).—A metabolic comparison of the effects of feeding on "sanatogen" with other forms of diet; some small differences in detail are noticeable.

W. D. H.

Assimilation of Proteid in Animals. EMIL ABDERHALDEN and FRANZ SAMUELY (*Zeit. physiol. Chem.*, 1905, 46, 193—200).—Recent research shows that the proteids peculiar to each animal are built up from the simple cleavage products of the proteid in the diet. The biological reaction shows the absence of any foreign proteid in the blood. A horse was bled, and after a hunger interval was fed on gliadin, which yields 36.5 of glutamic acid and 2.37 of tyrosine per cent. These numbers are very different from those obtained from the normal proteids of serum. But in the serum proteids of the new blood the horse made, the proportion of these products remained the same, and was not influenced by the different proportion in the food-proteid. It is not improbable that the liver as well as the intestinal wall plays a part in proteid synthesis.

W. D. H.

Vegetarianism. WILHELM CASPARI (*Pflüger's Archiv*, 1905, 109, 473—595).—A very complete study of the subject from several points of view. In the portion dealing with new researches, several experiments were made on human beings, and a complete record kept of their metabolic history. The most severe experiment lasted for ninety-six days on a man who weighed 53 kilos.; at the end of the time he weighed 40 kilos., and in his photograph appears like a skeleton; his main diet was apples and grapes. A pure vegetarian diet is inappropriate, because (1) it is badly absorbed, especially so far as proteids are concerned; (2) it is irritative to the alimentary canal; and (3) because of its large volume. These evils can, to a certain extent, be overcome by the use of certain preparations, but the small proteid intake appears to be insuperable.

W. D. H.

Autolysis. O. SCHUMM (*Beitr. chem. Physiol. Path.*, 1905, 7, 175—203).—Details are given of the products of autolysis in the tissues (especially spleen and bone marrow) of cases of leucæmia. In this disease, a proteolytic ferment occurs in the blood, which resembles trypsin in its activities, not pepsin as in some cases of this disease.

W. D. H.

The Condition of Living Substance. HUGO FISCHER (*Zeit. physiol. Chem.*, 1905, 46, 206—208).—Polemical against E. Buchner on the nature of the chemical processes of life, and as to how far the action of enzymes is to be considered a portion of the chemistry of life (compare Buchner and Antoni, this vol., ii, 472).

W. D. H.

Cholesterol Esters in the Brain. R. BÜNZ (*Zeit. physiol. Chem.*, 1905, 46, 47—51).—Baumstark (Abstr., 1885, 918) stated that the brain contains not only cholesterol, but cholesterol esters as well. In the present research, this is not confirmed; the ethereal extract contains no esters of cholesterol with higher fatty acids, or any other compounds of cholesterol from which cholesterol is separated by saponification.

W. D. H.

The Ereptic Power of Tissues as a Measure of Functional Capacity. HORACE M. VERNON (*J. Physiol.*, 1905, 33, 81—100).—The erepsin in the tissues of guinea-pig, cat, and rabbit increases *in utero* and for a few days after birth; then it remains constant. The increase is 5- or even 10-fold in kidney and liver, but slight in muscle. Feeding with meat in cats doubles the amount in spleen and liver, but does not affect other tissues. The distribution of erepsin in the alimentary canal is unequal; on a mixed or meat diet in cats, the duodenum is richest in the ferment; on a bread and milk diet, this falls, and the amount in the large intestine rises. In the herbivorous rabbit, the alimentary canal is altogether poorer in erepsin, especially in the duodenum. Hibernation lessens the erepsin in spleen, liver, and kidney, but not in brain or muscle. Disease, if accompanied by wasting, has the same effect.

W. D. H.

Mytolin, a Proteid from Muscle. W. HEUBNER (*Chem. Centr.*, 1905, ii, 1106; from *Arch. exp. Path. Pharm.*, 53, 302—312).—From rigorized horse-flesh, ammonia or 10 per cent. sodium chloride solution extracts a proteid matter named *mytolin*. When, by dialysis, the concentration of the salt solution is reduced to 2—3 per cent., it is precipitated in a comparatively insoluble form. By further dialysis, a globulin is precipitated. By the action of carbon dioxide and repeated solution in very dilute sodium carbonate, a part of the globulin is transformed into mytolin. Neutralisation of a saline extract of muscle precipitates mytolin, but leaves the globulin in solution.

W. D. H.

Hexone Bases of Liver Tissue. ALFRED J. WAKEMAN (*J. exper. Med. New York*, 1905, 7, 292—307. Compare this vol., ii, 467).—The results reported show that in degenerating liver tissue, chemical changes in the cells lead to a diminution of the hexone bases, but especially of arginine. How much arginine passes into the urine, or is acted upon by arginase, is uncertain. The changes during degeneration have the same general direction as in *post-mortem* autolysis.

W. D. H.

Grafting of the Thymus in Animals. LEONARD S. DUDGEON and A. E. RUSSELL (*Trans. Path. Soc. London*, 1905, **56**, 238—250).—The experiments were undertaken with the idea of observing whether grafting of the thymus gland would produce any alteration in the blood, or any condition resembling lymphatism, in which the thymus is known to play a part. The results were negative. W. D. H.

Lanocerin. FRANZ RÖHMANN (*Zentr. Physiol.*, 1905, **19**, 317—320).—Lanocerin is the name given to a new constituent of wool-fat, from which it can be prepared by boiling with methyl alcohol and then extracting the residue with ether. It is precipitated from this solution by alcohol. By boiling with alcoholic potash, the potassium salt of lanoceric acid (Darmstädter and Lipschutz, *Abstr.*, 1896, i, 522) is obtained. Lanocerin is an inner anhydride of this acid. The carnaubic acid of the same authors (*Abstr.*, 1896, i, 346; 1897, i, 180) is probably an impure product. The sebaceous glands yield a substance named *dermocerin*, the nature of which is uncertain. The anal glands do not secrete cholesterol, but an ester of octadecyl alcohol named *pennacerin*. The relationship of such substances to cholesterol and oleic acid is discussed. W. D. H.

Local Anæsthesia produced by Alypin. E. IMPENS (*Pflüger's Archiv*, 1905, **110**, 21—87).—The hydrochloride of alypin [tetramethyl-diaminoethyl-dimethylcarbinyl benzoate, $\text{OBz} \cdot \text{C}(\text{Et})(\text{CH}_2 \cdot \text{NMe}_2)_2$] is recommended as a local anæsthetic; it is at least as powerful as cocaine, and much less toxic. It does not produce mydriasis or any interference with accommodation. W. D. H.

Contractile Mechanism of the Gall-bladder. FRANCIS A. BAINBRIDGE and H. H. DALE (*J. Physiol.*, 1905, **33**, 138—155).—The rhythmic contractions of the gall-bladder are increased by section of the splanchnic nerves or by the intravenous injection of chrysotoxin. Stimulation of these nerves or injection of adrenaline causes relaxation. The vagus contains motor fibres which are paralysed by atropine. Bile salts, amyl nitrite, and atropine cause relaxation; pilocarpine and peptone cause an apparent contraction, due to the mechanical effect of swelling of the liver. The anæmia caused by compression of the aorta produces a rapid fall in the tone of the muscle of the gall-bladder. W. D. H.

A New Nitrogenous Constituent of Normal Human Urine. PAUL HÁRI (*Zeit. physiol. Chem.*, 1905, **46**, 1—8).—The zinc, silver, and cadmium compounds of a new constituent of the urine, precipitable therefrom by a 10 per cent. solution of phosphotungstic acid, were prepared and analysed. It contains carbon, hydrogen, nitrogen, and oxygen, but has not yet been isolated from its metallic compounds. It is not urobilin, but appears to have a possible relationship to Garrod's urochrome. W. D. H.

Excretion of Sugar after Administration of Alanine in Dogs without a Pancreas. MARCO ALMAGIA and GUSTAV EMBEN (*Beitr. chem. Physiol. Path.*, 1905, **7**, 298—310).—After extirpation of the

pancreas, the sugar which appears in the urine is considered to originate solely from carbohydrate material which is newly formed in the body. Alanine produces such a new formation of carbohydrates.

W. D. H.

Precipitability of Carbohydrates in Urine by Lead Acetate.

OSCAR ADLER and RUDOLF ADLER (*Pflüger's Archiv*, 1905, 110, 99—103. Compare this vol., ii, 337).—Proofs are adduced that lævulose may occur in the urine, and is partially precipitated (like arabinose and dextrose) by lead acetate.

W. D. H.

A Non-dialysable Proteid-like Constituent of Human Urine.

EMIL ABDERHALDEN and FRITZ PREGL (*Zeit. physiol. Chem.*, 1905, 46, 19—23. Compare this vol., ii, 467).—Urine contains a substance which yields glycine and phenylalanine on decomposition and appears to belong to the polypeptides.

W. D. H.

The Globulin of Albuminous Urine. A. W. SIKES (*J. Physiol.*, 1905, 33, 101—105).—In albuminous urine, the globulin increases somewhat on keeping at the expense of the albumin. The change occurs more readily in alkaline urine, and is probably not due to bacterial action. Albumose added to globulin solutions does not increase the amount of the latter substance. Electrical currents passed through the urine increase the globulin probably by heating the urine.

W. D. H.

The Chromogen of so-called Scatole-red in Normal Human Urine. J. PH. STAAL (*Zeit. physiol. Chem.*, 1905, 46, 236—262).—The chromogen of the so-called scatole-red in normal human urine is not a conjugated sulphate (for instance, of glycuronic acid). It is not a derivative of scatole in the chemical sense of that term, but is identical with the urorosein of Nencki and Sieber.

W. D. H.

A Prehistoric Egyptian Calculus. SAMUEL G. SHATTOCK (*Trans. Path. Soc. London*, 1905, 56, 275—290).—The examination of the calculus, which was obtained from a tomb of date 4800 B.C., showed it to consist of uric acid coated with phosphates; calcium oxalate was absent. A second calculus, probably renal, and 600 years later in date, was found to consist of calcium carbonate, phosphate, and oxalate.

The paper contains much of archaeological interest, especially with regard to the diseases and diet of the ancient Egyptians. No Bilharzia ova, the chitinous nature of the capsules of which would render them likely to be well preserved, were found in either stone. The second stone, however, contained numerous mould conidia, but attempts to cultivate these were fruitless.

W. D. H.

Virulence and Immunising Power of Micro-organisms.

RICHARD P. STRONG (*J. Exper. Med. New York*, 1905, 7, 229—264).—From experiments on two strains of cholera vibrio differing in virulence, it is shown that the number or the avidity of the bacterio-

lytic receptors possessed by a bacterium is proportional to its virulence. The agglutinable receptors are not necessarily present in the same proportion. The virulent organism possesses more toxic haptophore groups than the avirulent. Immunity produced by injecting dead organisms is proportional to their original virulence, but if the living organisms are used the proportion is not so direct. W. D. H.

Stimulins. W. B. LEISHMAN (*Trans. Path. Soc. London*, 1905, 56, 344—355).—The favouring effect of the addition of immune serum on the phagocytic action of leucocytes was originally attributed by Metschnikoff to a stimulating effect on the leucocytes, and the term *stimulin* was coined by him as a name for the substance in the serum to which the effect is due. In the present experiments, serum from cases of Malta fever and typhoid fever (but not normal serum) was found to possess the power of increasing the phagocytic activity of the leucocytes on the specific bacilli of those diseases. These substances are thermostable, withstanding a temperature of 60° for fifteen minutes. The increased phagocytosis may be in part due to the presence of agglutinins or of immune substance in the serum. The view is held that the main effect is a stimulating one on the leucocytes, and not due to the addition of an opsonin to the bacilli. Wright's hitherto described opsonins are destroyed by a temperature of 60°. It is, however, admitted that there may be a class of opsonins which are thermostable, a view Metschnikoff appears now also inclined to accept.

W. D. H.

[**Glycosuria**]. EDUARD PFLÜGER (*Pflüger's Archiv*, 1905, 110, 1—20).—Polemical against Minkowski.

W. D. H.

Experimental Glycosuria. FRANK P. UNDERHILL (*J. Biol. Chem., New York*, 1905, 1, 113—130. Compare this vol., ii, 187).—The glycaemia provoked by piperidine, pyridine, coniine, curare, nicotine, morphine, ether, chloroform, carbon monoxide, pyrogallol, &c., is not due to any specific action on any particular organ, such as the pancreas, but to their action in producing dyspnoea. If oxygen is also administered, it does not appear. Adrenaline diabetes cannot, however, be explained in this way.

W. D. H.

Opsonic Content of Blood Serum in Health and in Lupus. WILLIAM BULLOCK (*Trans. Path. Soc. London*, 1905, 56, 334—344).—Films made from blood mixed with tubercle bacilli were prepared and examined according to Wright's technique. The bacilli are counted in the leucocytes, and an average per leucocyte struck. If this is done after admixture with (1) an abnormal and (2) a normal serum, the average for leucocyte in the first case divided by that in the second is called the opsonic index. In 86 healthy people, the index was 0.97, the extremes being 0.8 and 1.2. In tuberculosis of the skin (lupus), the average was 0.75 in 150 cases. In 75 per cent. of these, the index was below the lowest normal limit, 0.8, and in 27 cases below 0.5; in 3 cases as low as 0.2. If the index is well below the normal, Finsen light treatment is of little or no benefit. The ultra-

violet rays have but little penetrative power, and probably exert no potent effect on tubercle bacilli. The healing properties in cases with high opsonic index are due to a reaction set up in the tissues and to the congestion and exudation that follow exposure to the rays.

W. D. H.

Behaviour of Leucocytes in Malignant Growths. J. E. FARMER, J. E. S. MOORE, and C. E. WALKER (*Trans. Path. Soc. London*, 1905, 56, 377—380).—In the early stages of a cancerous growth, there is marked activity among, and increase of, leucocytes, and there is evidence that the new growth does not originate from a single cell or even from a few cells, but is evolved by the direct conversion of normal cells into those of a malignant type. The tissue cells take up the leucocytes, but neither are injuriously affected or eventually destroyed, and both continue to divide mitotically; both nuclei pass through the mitotic evolution either on separate spindles or the spindle figures may become confused, as occurs in the first cleavage of the ovum. The two sets of chromosomes are confusedly distributed between the daughter nuclei, and the process may thus be compared to fertilisation. The reduction of chromosomes so characteristic of neoplastic cells must occur later.

W. D. H.

Metabolism in Osteomalacia. J. E. GOLDTHWAIT, C. F. PAINTER, R. B. OSGOOD, and FRANCIS H. MCCRUDDEN (*Amer. J. Physiol.*, 1905, 14, 389—402).—Metabolism experiments on a girl aged sixteen suffering from osteomalacia were carried out during two periods: (1) before, and (2) after castration. There is first a decalcification of the bony tissue; the calcium is replaced partly by magnesium, but probably chiefly by an organic substance rich in sulphur, but poor in phosphorus, similar to, but not exactly like, the normal organic matrix. Castration checks the progress of the disease, and the lost bony material is replaced.

W. D. H.

The Opsonic Index in Phthisis. HAROLD MEAKIN and CHARLES E. WHEELER (*Brit. Med. J.*, 1905, ii, 1396—1397).—The observations show the great variations in opsonic index in cases of pulmonary tuberculosis, and even in the same case, especially during the early stages of the disease. When the case becomes chronic, the opsonic index is fairly stationary; if it is then one or over, prognosis is better than when it is below unity.

W. D. H.

Enzymes and Anti-enzymes of Exudates. EUGENE L. OPIE (*J. Exper. Med. New York*, 1905, 7, 316—334).—The serum of an inflammatory exudate inhibits the action of the proteolytic enzymes contained in the leucocytes; the anti-enzyme doubtless passes from the blood into the exudation. In late stages of inflammation, this inhibiting action is lessened. The anti-enzyme is destroyed by heating at 75°.

The proteolytic enzymes of the leucocytes act in both an acid and alkaline medium, but are more efficient in the latter. The action of the anti-enzyme is favoured by an alkaline, and completely lost in an acid medium.

W. D. H.

[Physiological] **Action of Barium Chloride and of Barutine.** H. BRAT (*Chem. Centr.*, 1905, ii, 1189; from *Berl. klin. Woch.*, 42, 1219—1225).—"Barutine" is the double salt formed by the combination of barium theobromine with sodium salicylate. It is a white, crystalline powder and is soluble in water. Barium theobromine, prepared by the action of barium chloride on sodium theobromine, is insoluble in water. The preparation contains 9.5 per cent. of barium, 25.5 of theobromine, 50 of sodium salicylate, and about 10 of water and sodium chloride; since it is faintly alkaline, it requires to be kept in an atmosphere free from carbon dioxide. Whilst a dose of 0.113 gram of barium chloride per kilogram of body-weight is fatal to dogs when administered either internally or subcutaneously, barutine is at least nine times less poisonous. Experiments on the physiological action and therapeutic application of barutine as a diuretic have also been made. E. W. W.

Action of Adrenaline on Cerebral Vessels. CARL J. WIGGERS (*Amer. J. Physiol.*, 1905, 14, 452—465).—Perfusing the isolated brain under constant pressure and temperature and recording the venous outflow was the method adopted. Addition of adrenaline to the perfusion fluid lessens the outflow, owing no doubt to constriction of the vessels which the drug produces here as elsewhere. The existence of vaso-motor nerves in the cerebral blood-vessels is thus proved experimentally. W. D. H.

Action of Synthetical Substances allied to Adrenaline. OTTO LOEWI and HANS MEYER (*Chem. Centr.*, 1905, ii, 1111—1112; from *Arch. exp. Path. Pharm.*, 53, 213—226).—Stolz's methylaminoacetyl catechol, probably the corresponding ketone to adrenaline, has a similar but weaker physiological action. Of Stolz's other products, the simple amino-ketones show the strongest action, that of the ethyl being more marked than that of the methyl compound. Dialkylamino-ketones, monoethanolamino-ketones, and phenylaminoacetyl catechol are inactive; piperidinoacetyl catechol has only a weak action. Reduction of the amino-ketone produces an amino-alcohol not yet obtained pure, but similar to adrenaline. The active products like adrenaline act on blood pressure, respiration, and the iris muscles, and produce diabetes. Given subcutaneously they also cause the same results. Hydrochlorides of some of these bases were prepared in crystalline form. W. D. H.

Hippuric Acid Synthesis. WILHELM WIECHOWSKI (*Beitr. chem. Physiol. Path.*, 1905, 7, 204—272).—A study of the pharmacological action of benzoic acid given in various ways to rabbits. The amount given is not wholly excreted as hippuric or benzoic acids; the longer it remains in the body the greater is the amount of hippuric acid synthetically formed. Glycine as an intermediate metabolic product is considered at some length. More than half the urea-nitrogen is believed to pass through the glycine stage. Descriptions of analytical methods and references to literature are given in full. W. D. H.

Physiological Action of Physostigmine. W. HEUBNER (*Chem. Centr.*, 1905, ii, 1111; from *Arch. exp. Path. Pharm.*, 53, 313—330).—Experiments on frogs, mammals, and man show that no immunity can be produced to physostigmine. In a dog, that received 60 mg. in 19 days, only 2 mg. were recovered in the urine. Physostigmine-blue, a derivative of physostigmine, is not poisonous in small doses; larger doses paralyse the heart and central nervous system in frogs. Another derivative, rubreserin, is inactive. The alkaloid itself has the constitution $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{13}\text{H}_{15}\text{N}\cdot\text{OH}$. It splits into eseroline and rubreserin; the latter in alkaline solution is changed into physostigmine-blue, the composition of which is unknown. It forms brown, amorphous products on drying and evaporation. W. D. H.

Influence of Thyroid Feeding on Poisoning by Acetonitrile. REID HUNT (*J. Biol. Chem.*, 1905, 1, 33—44).—Proteids increase the susceptibility of mice to acetonitrile, whilst thyroid feeding (and potassium iodide to a slight extent) decreases it. Thyroid has no antagonistic action towards sodium nitroprusside or free hydrocyanic acid. Feeding on parathyroids has the opposite effect to thyroid feeding. W. D. H.

Action of Certain Poisons on the Isolated Small Intestine of Dogs and Rabbits. K. KRESS (*Pflüger's Archiv*, 1905, 109, 608—620).—The work was carried on by Magnus' method. Nicotine causes first inhibition, then stimulation; larger doses produce paralysis. Certain differences are noticeable in detail in different animals. Atropine in the cat, but not in the dog or rabbit, acts antagonistically to nicotine. There are also differences in the antagonistic actions of physostigmine and atropine and of pilocarpine and atropine. The action of a number of other poisons (strophanthine, apocodeine, barium chloride, adrenaline, &c.) was also studied.

W. D. H.

Isoform, a New Antiseptic. BERNHARD HEILE (*Vollmann's Sammlung klin. Vorträge, Leipzig*, No. 388, 149—164); WEIK (*Med. Klinik., Berlin*, 1905, No. 19).—Isoform (*p*-iodoanisole) is recommended as a local antiseptic, being better than iodoform; it is non-irritating, odourless, and non-toxic.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Metals on Fermenting Liquids. LEOPOLD NATHAN, ARTHUR SCHMID, and WILLY FUCHS (*Centr. Bakt. Par.*, 1905, ii, 15, 349—352. Compare Abstr., 1904, ii, 505, and this vol., ii, 340).—The contact of beer worts before and during the fermentation with metals, whether copper, iron, or tin, should be avoided as much as possible.

N. H. J. M.

Origin of Fusel Oil. An Alcohol-producing Bacterium. HANS H. PRINGSHEIM (*Centr. Bakt. Par.*, 1905, ii, 15, 300—321).—Fusel oils produced from different materials are very similar and contain, besides amyl alcohol, considerable amounts of propyl and isobutyl alcohols and small amounts of other alcohols. Normal butyl alcohol is not present.

All bacteria which produce higher alcohols produce normal butyl alcohol, whilst amyl alcohol has not been detected. Emmerling's potato bacteria produces propyl alcohol, the potato bacillus isopropyl alcohol, Grimbert's *B. orthobutyricus* isobutyl alcohol, whilst a number of bacteria produce normal butyl alcohol, together with butyric acid. Bacteria which produce alcohols (except Winogradski's *Clostridium Pasteurianum*) produce far more butyric acid than corresponds with the composition of fusel oil.

The view that fusel oil is produced by bacteria is therefore incorrect ; the higher alcohols are probably formed by the decomposition of yeast-proteid.
N. H. J. M.

Action of the Rennet Ferment on Milk and Casein. ERNST LAQUEUR (*Biochem. Centr.*, 1905, 4, 333—347).—A résumé, with bibliography, of the more important work on the subject.

N. H. J. M.

Apparatus for the Cultivation of Anaërobic Bacteria and for the Estimation of the Oxygen-minima for Germination, Growth, and Spore-production of Bacteria. ARTHUR MEYER (*Centr. Bakt. Par.*, 1905, ii, 15, 337—349).—The apparatus, consisting of an air-pump with a new form of drying tube, cylindrical vacuum vessels, and manometer, is described with sketches.
N. H. J. M.

Acidifying and Fermenting Yeast Mash. (Behaviour of Bacillus Delbrücki at Different Temperatures.) WILHELM HENNEBERG (*Centr. Bakt. Par.*, 1905, 15, ii, 260—265 ; from *Zeit. Spiritusind.*, 1905, No. 26—29).—The bacilli from mash cultures heated at 51° failed to grow both at higher and lower temperatures, being weakened chiefly by the acid present. In presence of calcium carbonate, no weakening was observed. Cultures heated at 38° without calcium carbonate showed a good growth after four days, although 1·2 per cent. of lactic acid was present. The mash, which had been heated at 51°, contained 0·9 per cent. of acid. The weakening is, therefore, due both to acid and to the high temperature.

The greater the number of cells sown, the greater the development and the shorter the cells. The length of the cells is also affected by the temperature ; at 50°, the cells are short, at 40°, much longer, whilst at 30° the cells are extremely long.
N. H. J. M.

Influence of Temperature on the Assimilation of Carbon Dioxide. ARISTIDES KANITZ (*Zeit. Elektrochem.*, 1905, 11, 689—690).—From the experiments of Matthaei (*Abstr.*, 1904, ii, 70) it is shown that the rate of assimilation of carbon dioxide by green leaves

increases with the temperature in the ratio commonly found for chemical reactions.

Temperature.	Assimilation rate.	Increase for 10°.
0	1·75	—
10	4·2	2·40
20	8·9	2·12
30	15·7	1·76
37	23·8	1·81

From 37° to the temperature at which the leaf is killed, the rate rapidly diminishes. T. E.

Physiological Processes of Green Leaves, with Special Reference to the Interchange of Energy between the Leaf and its Surroundings. HORACE T. BROWN and FERGUSSON ESCOMBE (*Proc. Roy. Soc.*, 1905, *B*, 76, 29—111. Compare Abstr., 1902, ii, 682).—The rate of carbohydrate formation (assimilation) in a leaf surrounded by an atmosphere containing about the normal proportion of carbon dioxide (0·03 per cent.) is determined by passing a known volume of air over the leaf and finding by analysis the proportion of carbon dioxide present before and after the experiment. Since one part by weight of carbon dioxide corresponds with about 0·64 part by weight of carbohydrate, the amount of the latter produced in a given time can readily be calculated. The results obtained by this method are much lower than those deduced by Sachs' method (determination of the variations in dry weight of known areas of leaf lamina), and the authors, from their experiments, draw the conclusion that there are inherent errors in the latter method which render it unsuitable for determining the rate of assimilation.

As an illustration of the results obtained, it was found that a sunflower leaf, exposed to strong diffused light, assimilated 0·00392 gram of carbohydrate per square decimetre per hour. The rate of assimilation under similar conditions is about 45 per cent. greater in detached than in attached leaves; this is due, in all probability, to the stomata being more widely open in the former case.

The question of the energy relations of the leaf is fully discussed. For this purpose it is necessary to know the amount of solar energy incident on the leaf, the amount absorbed, and the amount of heat lost by radiation, convection, &c., in unit time, as well as the energy changes associated with the more important physical and chemical changes going on in the leaf, such as the evaporation of water, carbohydrate formation, and the process of respiration. The influence of the rate of motion of the air on some of these factors is taken into account.

The incident solar energy is measured by a Callendar radiometer and recorder, and the proportion absorbed determined with the same instruments by interposing the leaf and measuring the amount transmitted. The amount of heat developed in respiration is calculated from the amount of carbon dioxide given off on the assumption that carbohydrates are undergoing oxidation (Brown and Morris, *Trans.*,

1893, 63, 671). The energy absorbed in assimilation is calculated from the amount of carbon dioxide absorbed and the average heat of formation of the synthesised carbohydrates. The energy used up in the vaporisation of water is calculated from the amount of vapour evolved in a given time (determined directly) and the latent heat of vaporisation. The following results, obtained with a sunflower leaf, illustrate the relative magnitudes of these factors :

Energy used for assimilation	0.66
„ „ „ vaporisation of water . . .	48.39
<hr/>	
Total energy expended in internal work	49.05
Solar radiant energy transmitted by leaf	31.40
Energy lost by radiation, convection, &c .	19.55
<hr/>	
Total incident energy	100.00

The leaf is, therefore, a very wasteful transformer of energy, as in the example quoted only 0.66 per cent. is used for the production of formative material.

When the solar energy absorbed is greater than the energy expended in internal work, the leaf comes to equilibrium at a temperature higher than its surroundings. The temperature difference can be found by dividing the energy lost by radiation, convection, &c., by the "thermal emissivity" of the leaf (the energy lost by radiation, convection, &c., when the leaf is at a temperature 1° above its surroundings), a special method for determining the latter factor having been devised. When, owing to active transpiration, the energy expended in internal work is greater than the solar energy absorbed, the leaf takes up heat from the atmosphere and comes to equilibrium at a temperature slightly lower than that of its surroundings.

The solar energy can be reduced to a fraction of its value without seriously affecting the rate of assimilation, so that even in diffused daylight the available energy is more than sufficient to give the maximum effect ; assimilation is, under ordinary conditions, limited by the small concentration of the carbon dioxide.

Tables showing the distribution of the energy under varying conditions are given in the paper. G. S.

Occurrence of Alumina in Plants. HENRI PELLET and CH. FRIBOURG (*Ann. Chim. anal.*, 1905, 10, 373—376. See this vol., ii, 860).

Consumption of Odorous Products during the Maturation of the Flower. EUGÈNE CHARABOT and ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1905, [iii], 33, 1121—1128. Compare Abstr., 1904, ii, 837).—The authors have investigated the changes induced both in the amount and nature of the volatile oil produced by the sweet basil (*Ocimum basilicum*) as the result of systematically removing the flowers as these appear on the plant. The results are tabulated in the original, and show that the removal of the inflorescence leads (1) to an increase in the size of the stem of the plant, (2) to an increase in

the amount of oil produced per unit weight of plant substance, and (3) that the processes of fertilisation and fructification lead to the consumption of some of the odorous constituents or of intermediate substances from which these are produced.

T. A. H.

The Carbohydrates of Marine Algæ and their Products. JOSEF KÖNIG and J. BETTELS (*Zeit. Nahr. Genussm.*, 1905, 10, 457—473).—The general composition, the carbohydrates, and the products obtained on hydrolysis of various East Asiatic algæ are given. The composition of the different sea-weeds varies very considerably, the *Porphyra* group being rich in proteids, whilst *Laminaria*, *Cystophyllum*, and *Enteromorpha* contain from 6·66 to 10·87 per cent. of pentosans, the latter sea-weed also containing 16·52 per cent. of methylpentosans. In all, the percentage of ash is very high. *Porphyra*, from which the Japanese vegetable isinglass "Nori" is prepared, and *Gelidium*, which yields agar-agar, both give *i*-galactose and *d*-galactose, these anhydrides being also found in the products nori and agar-agar. The authors have examined samples of edible birds' nests and find that they contain but small quantities of substances which yield reducing sugars, only fructose being identified with certainty. The nests contained from 50 to 60 per cent. of nitrogenous substances resembling mucin, and it is perfectly legitimate to conclude that edible bird nests are produced from the vomit of sea-swallows.

W. P. S.

Constituents of the Fruits of *Copaifera Mopane*. CARL MAI and C. RATH (*Arch. Pharm.*, 1905, 243, 426—430).—Chloroform extracts from the seeds a balsam with the acid number 57·4 and saponification number 212. From this a small quantity of a substance crystallised which melts at 96°, is free from nitrogen and metals, and contains C 74·7, H 11·5 per cent. From an ethereal solution of the residual balsam, 5 per cent. aqueous sodium carbonate extracted *acids* of which the lead salts were in part soluble in ether; the acid corresponding to this portion was amorphous and formed a *barium* salt which contained Ba 36·1 per cent. The residual balsam was then hydrolysed with 5 per cent. potassium hydroxide solution, and the *acids* liberated; of these, one fraction crystallised from 70 per cent. alcohol and melted at 77°, but was not homogeneous; the residue was not homogeneous either.

C. F. B.

Root of *Rheum Rhaponticum*. ALEXANDER TSCHIRCH and U. CRISTOFOLETTI (*Arch. Pharm.*, 1905, 243, 443—457. Compare Hesse, Abstr., 1900, i, 41, and Gilson, *Bull. acad. roy. méd. Belg.*, 1903).—The powdered root of *Rheum rhaponticum*, of Austrian origin, was extracted with 70 per cent. alcohol, and the extract evaporated to small bulk and then extracted with ether. During the last operation, a substance separated identical with the substance described originally by Hornemann as *rhaponticin* (Hesse's rhapontin; Gilson's ponticin). This melts at 231°, has the composition $C_{21}H_{24}O_9 = OMe \cdot C_{20}H_{19}O_8(OH)_2$, forms a *diacetyl* derivative melting at 138°, gives an odour of oil of bitter almonds when it is warmed on a watch-glass with dilute nitric

acid, and is hydrolysed when heated cautiously with dilute sulphuric acid to dextrose and rhapontigenin (Gilson); it does not yield chrysamic acid when treated with nitric acid. Rhapontigenin has the composition $C_{17}H_{22}O_3 = OMe \cdot C_{16}H_{17}(OH)_2$; its *dibenzoyl* and *diacetyl* derivatives melt at $145-146^\circ$ and $110-112^\circ$ respectively.

The ethereal extract was evaporated, and the residue digested with cold 10 per cent. aqueous sodium carbonate. Chrysophanic acid remained undissolved, melting at $181-182^\circ$ and still containing 1.48 per cent. of methoxyl (for the substance which is completely freed from methoxyl, 5:8-dihydroxy-1-methylanthraquinone, which melts at 196° , the name of *chrysophanol* is proposed). From the alkaline solution, a yellow substance, $C_{16}H_{16}O_5 = OMe \cdot C_{15}H_{13}O_4$, melting at 216° , is obtained; this is presumably a *dihydroxymethoxymethyltetrahydroanthraquinone*. Neither emodin nor rhein could be detected.

The liquid remaining after the extraction with ether was hydrolysed with 3 per cent. alcoholic potassium hydroxide. The products were rheum-red, rheonigrin, dextrose, and an orange-red *dihydroxydimethyltetrahydroanthraquinone*, $C_{16}H_{16}O_4$, which melts at $195-196^\circ$ and forms a yellow *diacetyl* derivative melting at 205° .

After extraction with 70 per cent. alcohol, the material was extracted with 95 per cent. alcohol, which dissolved chrysophanic acid and an anthraglucoside which yielded *d*-glucose and dihydroxydimethyltetrahydroanthraquinone.

From a sample of the roots cultivated in Berne, dihydroxymethoxymethyltetrahydroanthraquinone, emodin, and rhein could not be isolated, and anthraglucosides were present only in small amount.

C. F. B.

The Existence of a Cyanogenetic Compound in *Thalictrum Aquilegifolium*. LEOPOLD VAN ITALIE (*J. Pharm. Chim.*, [vi], 22, 337-338).—The leaves of *Thalictrum aquilegifolium* contain a glucoside resembling phaseolunatin (compare Dunstan and Henry, *Abstr.*, 1904, ii, 71), for on hydrolysis with emulsin it yields hydrogen cyanide and acetone, one kilogram of the leaves producing 0.502 to 0.6 gram of hydrogen cyanide. The leaves of *Thalictrum flavum*, *T. minus*, or *T. glaucum* do not furnish hydrogen cyanide under the same conditions.

M. A. W.

Chemistry of the Scleroderms. MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1905, 26, 1109-1118. Compare *Abstr.*, 1903, ii, 567).—Unripe specimens of *Lycoperdon bovista* from the Pitztal, in Tyrol, were extracted with 96 per cent. alcohol at the ordinary temperature and again at the boiling point.

The first extract yielded tyrosine and a substance which contains $C = 40.59$, $H = 4.79$, $N = 26.24$ per cent.; it crystallises in sheaves of glistening, white needles, becomes yellow at 215° and dark brown at 240° , is easily soluble in aqueous sodium hydroxide, gives a yellowish-red coloration with concentrated sulphuric acid, forms an intense yellowish-brown solution when boiled with Moerner's tyrosine reagent, and when evaporated with dilute nitric acid yields a lemon-yellow residue, which darkens on treatment with ammonia and becomes

reddish-yellow on addition of sodium hydroxide. With silver nitrate in aqueous solution, it forms a transparent jelly, or in dilute solution a flocculent precipitate which becomes opaque on addition of baryta water; on addition of lead acetate, the aqueous solution becomes opaque, and in presence of a small quantity of ammonia forms a white, flocculent precipitate; with phosphotungstic acid in very dilute sulphuric acid solution, the substance forms a yellow, flocculent precipitate.

The second extract yielded (a) two substances melting at 158—159° and 163·5—164° respectively, which are closely related to ergosterol (compare Hofmann, *Inaug. Diss., Zurich*, 1901), crystallises in long needles or hexagonal plates, are easily soluble in hot ether or chloroform, and give the cholesterol reactions; and (b) a substance which contains C = 64·48, H = 11·41, N = 1·48 per cent., and belongs probably to the cerebroside group; it separates from acetic acid as a loose white powder, becomes yellow at 165°, melts at 180—200°, is decomposed by warm concentrated sulphuric acid, and when boiled with dilute sulphuric acid forms a substance which reduces Fehling's solution when heated.

G. Y.

Measure for the Action of Poisons on Plants. EDUARD VERSCHAFFELT (*Chem. Centr.*, 1905, ii, 1033; from *Arch. Néerland*, ii, 10, 1—7).—The fact that a dead cell does not increase, but rather decreases, in weight in water is utilised as a means of measuring the external influences sufficient to cause the death of cells.

The poisonous limit of copper sulphate after twenty-four hours' action on potato starch is between 0·03 and 0·05 per cent. Sodium chloride is poisonous in 2·34 per cent. solutions, whilst 1·75 per cent. is without action; in the case of parts of mangolds the strength has to be 3—5 times as great to exert a poisonous action. Potassium bromide and nitrate resemble sodium chloride; dextrose and sucrose act similarly in only slightly greater concentration. Addition of certain amounts of sodium chloride diminish the poisonous action of quinine hydrochloride, whilst larger amounts increase the poisonous action. The poisonous action of oxalic acid is partially neutralised by sodium chloride and also, in a less degree, by sucrose.

N. H. J. M.

Insensibility of Higher Plants towards their own Poisons. G. J. STRACKE (*Chem. Centr.*, 1905, ii, 1033—1034; from *Arch. Néerland*, [ii], 10, 8—61).—Tissues of higher plants may be insensible towards their own poisons, but this is not always the case. The same cells may be insensible towards other poisons than those to which they are accustomed. It is probable that in some cases poisonous liquids obtained from plants only become poisonous after their separation owing to the action of enzymes.

Of the various acids investigated, the most poisonous are hydrochloric and oxalic acids; the less poisonous acids, tartaric, citric, malic, and lactic acids, are about equal among themselves.

Alkaloids are only slightly poisonous towards higher plants; the most poisonous is quinine hydrochloride, and strychnine hydrochloride is more poisonous than the nitrate.

N. H. J. M.

Glyceria Fluitans, an almost forgotten Cereal. C. HARTWICH and G. HÅKANSON (*Zeit. Nahr. Genussm.*, 1905, 10, 473—478).—This grain is known under a variety of names, such as manna-grass, manna-millet, &c. A sample examined by the authors gave the following results: water, 13·54; proteids, 9·69; fat, 0·43; starch and sugar, 75·06; crude fibre, 0·21; ash, 0·61 per cent. Each grain is about 2·5 mm. long and has a semi-transparent white colour. The starch grains resemble those of the oat.
W. P. S.

Changes in the Nitrogen in Soils. F. LÖHNIS (*Centr. Bakt. Par.*, 1905, ii, 15, 361—365; from *Habilitationsschr. and Mitt. landw. Inst. Univ. Leipzig*, Heft 7, 1—103).—The decomposition of bone meal varies least according to the time of the year; nitrification, denitrification, and assimilation are more influenced, whilst the effect of season is most marked in the decomposition of urea and calcium cyanamide. Stubble has a distinct effect on denitrification and nitrogen assimilation, but not on the other changes. The effect of bringing the lower layers of soil to the surface was seen chiefly in diminished nitrification; the effect was less in the case of the decomposition of bone-meal and urea, and no effect was observed as regards nitrogen assimilation and the decomposition of calcium cyanamide.

The dryness in July was particularly injurious in connection with nitrification, nitrogen assimilation, and the decomposition of calcium cyanamide, but had practically no effect on denitrification and the decomposition of bone-meal and urea. For the uninterrupted continuance of the various changes in the soil, 60—80 per cent. of the water-holding capacity of the soil is required; for some changes 50 per cent. is too little.
N. H. J. M.

Transformations of Sodium Nitrate in the Soil of Sugar-beet Fields. JULIUS STOKLASA (*Zeit. Zuckerind. Böhm.*, 1905, 30, 1—8).—It was formerly thought that, when used as a fertiliser, sodium nitrate is only absorbed in small quantity by the surface soil, and that the amount of this salt not assimilated by the roots of plants is washed through into the sub-soil. The author finds that this view is erroneous, and that the sodium nitrate is assimilated also by algæ and bacteria, especially *Clostridium gelatinosum*, which are always present in soil in which sugar-beets have been cultivated, and which convert the nitrate into ammonia. The sub-soil never contains more than about half the amount of nitrogen present in the surface-soil in which the active bacteria are at work. The nitrogen of the nitrate is converted into organic and ammonia-nitrogen, the latter amounting to from 5 to 10 per cent. of the total nitrogen of the nitrate.
T. H. P.

[Manurial Experiments] at Marburg. EMIL HASELHOFF (*Chem. Centr.*, 1905, ii, 1043—1045; from *Landw. Jahrb.*, 34, 597—664. Compare this vol., ii, 650).—Calcium cyanamide acts more injuriously on seeds in sand than in soil, and on mustard more than on clover. When, however, the injurious substances have been decomposed in the

soil, the effect of calcium cyanamide is similar to that of sodium nitrate.

Basic slag-ammonia is of no practical importance owing to losses when kept. In four weeks there was a loss of 20·9 per cent. of the total nitrogen.

The immediate effect of basic slag, or bone-meal, and kainite is increased by mixing the manures before applying them to the soil. The after effect is somewhat diminished, but the total effect, over two years, is greater when the manures are mixed than when applied separately.

N. H. J. M.

Retrogression of Soluble Phosphates in Mixed Manures.

GEORGE GRAY (*Trans. Austral. Assoc. Sci.*, 1904, 157—161).—In a mixture of superphosphate and bone-dust, retrogression is slight and the citrate-soluble phosphoric acid increases at the expense of the insoluble phosphate. Bone-dust is the best form of tricalcium phosphate for mixing with superphosphate. Coral Queen guano reduced 7 per cent. of the soluble phosphoric acid in eighteen days. With Chesterfield guano, which contains much calcium carbonate (37·9 per cent.), retrogression was considerable, tricalcium phosphate being formed. Addition of basic slag resulted in 50 per cent. of the phosphoric acid being rendered insoluble in three hours, owing partly to the lime but more particularly to the oxides of iron. With slaked lime, retrogression was very rapid, and with ground limestone considerable. Kainite had only a slight effect, due chiefly to the magnesium salts.

N. H. J. M.

Analytical Chemistry.

A New Apparatus for Gas Analyses. BERNHARD NEUMANN (*Chem. Zeit.*, 1905, **29**, 1128).—A convenient (patented) portable apparatus for testing gases or their products of combustion in factories, &c.

For particulars, the original article and illustration should be consulted. L. DE K.

Improved Orsat Apparatus. A. BEMENT (*J. Amer. Chem. Soc.*, 1905, **27**, 1252—1255).—An improved Orsat apparatus is fully illustrated in the original. The chief distinguishing features are that the gas may be aspirated through the burette, and also that the pipette is so constructed that the absorbing reagent is sprayed or projected into the gas. L. DE K.

Improved Gooch Crucibles. H. VOLLERS (*Chem. Zeit.*, 1905, **29**, 1088).—The new crucible, made either of platinum or porcelain, has a cylindrical indentation in the bottom, the sides of which are perforated. These perforations run parallel with the plane of the actual bottom, so

that it is impossible for any particles of asbestos to be lost during the filtration.

L. DE K.

Quick Method for the Valuation of Fluorspar. A. W. GREGORY (*Chem. News*, 1905, 92, 184—185).—The carbon dioxide is estimated by the loss on ignition at a red heat of the dry fluorspar; the free silica by heating with hydrofluoric acid and the combined silica by heating with sulphuric acid and with hydrofluoric acid, the residue from the last treatment being converted into sulphate by the further action of sulphuric acid. This sulphate and also the fluoride from the second treatment are each weighed, and from these numbers and those for the carbon dioxide and total silica the amount of fluoride originally present is calculated.

D. A. L.

Apparatus for Estimating Sulphur in Iron and Steel. A. KLEINE (*Chem. Zeit.*, 1905, 29, 1129).—A slight modification of the apparatus previously described (*Abstr.*, 1903, ii, 694). The delivery tube dipping into the beaker or small Erlenmeyer flask containing the absorbent resembles a pipette, into the body of which has been placed a float. If regurgitation should take place, the float is pushed upwards by the inflowing liquid and so closes the orifice of the tube. The tube may be afterwards conveniently used as a stirring rod during the titration.

L. DE K.

Some Uses of Iodic Acid in Volumetric Analysis. TH. SCHUMACHER and E. FEDER (*Zeit. Nahr. Genussm.*, 1905, 10, 415—417).—Sulphurous acid may be estimated in foods, &c., by acidifying the latter with phosphoric acid and distilling in a current of carbon dioxide. The distillate is received in a flask containing potassium iodate solution and in connection with a second flask containing a little potassium iodide solution. The sulphur dioxide decomposes the iodate according to the equation: $2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 4\text{H}_2\text{SO}_4 + \text{I}_2$. After neutralising the sulphuric acid by the addition of calcium carbonate, the solution is titrated as usual with thiosulphate solution. If any iodine passes over into the second flask, the contents must not be mixed with the main distillate until after the calcium carbonate has been added.

Sodium thiosulphate solution may be standardised as follows: 0.1 gram of potassium iodate and 0.3 gram of potassium iodide are dissolved in 50 c.c. of water, 20 c.c. of *N*/10 sulphuric acid are then added, and the liberated iodine titrated with the thiosulphate solution.

To prepare *N*/10 iodine solution, 5 grams of potassium iodate and 25 grams of potassium iodide are dissolved in water. Exactly 100 c.c. of *N*/1 sulphuric acid are added and the mixture diluted to 1 litre.

W. P. S.

An Improved Method for Estimating Nitrogen in Amino-acids. VLADIMIR STANĚK (*Zeit. physiol. Chem.*, 1905, 46, 263—272).—The reaction described by Tilden between nitrosyl chloride and amino-acids may be used for quantitative purposes. The apparatus employed is described and figured, and examples are given of the exactitude of the method.

W. D. H.

Estimation of Phosphoric Acid by means of Ammonium Phosphomolybdate. II. GREGORY P. BAXTER and ROGER CASTLE GRIFFIN (*Amer. Chem. J.*, 1905, **34**, 204—217).—The conclusion arrived at in the previous paper (*Abstr.*, 1903, ii, 180), that it is possible to obtain a precipitate of constant composition and in a fit state for weighing, is confirmed. For the exact composition of the ammonium phosphomolybdate, the first paper should be consulted. It is essential that the phosphate solution should be added to the molybdate solution and not the reverse; otherwise the composition of the compound will be altered. The precipitation should take place in the cold, but if much potassium is present this replaces part of the ammonium in the precipitate; this, however, may be again replaced by ammonium on heating the precipitate with ammonium nitrate solution, thereby converting it into triammonium phosphomolybdate. According to the conditions of precipitation, ammonium phosphomolybdate occludes varying amounts of molybdic acid and ammonium molybdate. No method of estimating phosphoric acid is accurate unless notice is taken of such admixture.

The author further objects to Pemberton's titration of the yellow precipitate with standard potassium hydroxide, as the presence of ammonia affects the indicator phenolphthalein. Moreover, 24, not 23, mols. of alkali neutralise 1 mol. of ammonium phosphomolybdate.

L. DE K.

A Rapid Volumetric Method for the Estimation of Phosphoric Acid. W. B. HIRT and FRED W. STEEL (*Proc. Soc. Chem. Ind. Victoria*, 1905, 14—19).—*Total Phosphoric Acid.*—Two grams of the sample, charred if necessary, are heated with 5 c.c. of acid mixture (sulphuric acid, 250 c.c.; nitric acid, 150 c.c.; water, 100 c.c.) until sulphuric acid fumes are abundantly evolved. When cold, the mass is treated with about 150 c.c. of water and transferred to a 200 c.c. flask, 40 c.c. of alcohol are added, and the whole is made up to the mark. Twenty-five c.c. of the filtrate (0.25 gram sample) are then titrated as follows: the solution is neutralised first with normal sodium hydroxide, and towards the end with *N*/10 sodium hydroxide, using methyl-orange as indicator. Ten c.c. of absolutely neutral sodium citrate solution of sp. gr. 1.151 are added, and the titration is continued with a special sodium hydroxide solution (prepared by diluting 35.52 c.c. of normal sodium hydroxide to 1000 c.c.), using phenolphthalein as indicator. Each c.c. of this solution represents 1 per cent. of phosphoric anhydride.

Phosphoric Acid Soluble in Water.—Two grams are treated as usual on a filter with 200 c.c. of water. When about 50 c.c. have collected, 1 c.c. of 10 per cent. sulphuric acid is added to prevent phosphatic precipitation. Finally, 25 c.c. of the solution are titrated as directed.

Phosphoric Acid Insoluble in Water and Ammonium Citrate.—The residue left on treatment with water is treated with solution of neutral ammonium citrate of sp. gr. 1.09 and burnt to a white ash. This is then heated with 5 c.c. of an acid mixture (sulphuric acid, 60 c.c.; nitric acid, 100 c.c.; water, 140 c.c.) until sulphuric fumes appear. After making up to 100 c.c. with water, 25 c.c. of the

solution (0.5 gram) are titrated as above. The burette reading should be divided by 2, so as to indicate the percentage of phosphoric anhydride.

The process, which is a modification of that recommended by Littmann (*Abstr.*, 1889, ii, 330), gives results fully agreeing with those obtained by the gravimetric methods. L. DE K.

Estimation of Arsenic as Magnesium Pyroarsenate. JUAN FAGES VIRGILI (*Ann. Chim. Phys.*, 1905, [viii], 6, 394—407).—A *résumé* of work already published (compare this vol., ii, 652). M. A. W.

Detection and Estimation of Arsenic and Antimony in Presence of Organic Matter. F. A. NORTON and A. E. KOCH (*J. Amer. Chem. Soc.*, 1905, 27, 1247—1252).—The process is based on the destruction of the organic matter by heating with sulphuric acid in a Kjeldahl flask. The residue contains the arsenic or antimony in the lower state of oxidation, and this may then be at once titrated with *N*/10 iodine in the usual manner.

If the amount of arsenic or antimony is but small, a large quantity of the material must first undergo a preliminary treatment in the case of arsenic with nitric and sulphuric acids, or in the case of antimony with hydrochloric acid and potassium chlorate. A definite quantity of the solution thus obtained is then boiled in a Kjeldahl flask with sulphuric acid in order to destroy completely the last traces of organic matters.

Traces of arsenic are best estimated by the "mirror" method.

L. DE K.

New Method for the Determination of Atmospheric Carbon Dioxide, based on the Rate of its Absorption by a Free Surface of a Solution of an Alkali Hydroxide. HORACE T. BROWN and FERGUSON ESCOMBE (*Proc. Roy. Soc.*, 1905, B, 76, 112—117).—When a current of air containing a constant proportion of carbon dioxide is drawn over a free surface of a solution of sodium hydroxide, the rate of absorption increases with the velocity of the air current up to a certain speed, beyond which it remains constant. Further, the rate of absorption is proportional to the partial pressure of the carbon dioxide within fairly wide limits. On these facts, a method for estimating carbon dioxide in the atmosphere has been based, which has the advantage that it is unnecessary to measure the volume of air passed through the apparatus.

The air is aspirated through the apparatus at a rate greater than that required for maximum absorption and, by being passed through a perforated plate, is caused to impinge in a turbulent stream on the surface of a standardised solution of sodium hydroxide, which is titrated after the experiment. The constant of the apparatus having been determined once for all by a preliminary experiment in which the air is measured, the proportion of carbon dioxide in a sample of air can be calculated from the time during which the current has passed and the amount of gas absorbed, a correction being applied for the effect of change of temperature on the rate of absorption.

Samples of air containing 0.04 to 18 parts of carbon dioxide in 10,000 have been analysed by this method, and the results agree very satisfactorily with those obtained by the very accurate method of Reiset. G. S.

A Simplified Method for the Estimation of Potassium. FRIEDRICH KLINKERFUES (*Chem. Zeit.*, 1905, 29, 1085—1086).—Some further observations on the process previously described (this vol., ii, 204). The solution of the platinichloride need not always be evaporated to dryness with the formic acid in order to get a firm coating of platinum. Ammonium salts behave similarly. If both potassium and ammonium have to be estimated, the latter must be first expelled by boiling with water containing magnesium or sodium hydroxide and titrating the distillate. The residue in the flask may then be used for estimating the potassium in the way described. L. DE K.

Use of the Rotating Anode and Mercury Cathode in Electro-analysis. I. LILY G. KOLLOCK and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1905, 27, 1255—1269).—A lengthy paper dealing with the electrolytic deposition of zinc, copper, nickel, cobalt, chromium, and iron, fully illustrated by tables and curves. For working details, the original paper should be consulted.

The decomposition cell is a tube 3.5 cm. in diameter and 7.5 cm. in height made from a test-tube. The bottom of the tube is softened over the blow-pipe, and a platinum wire 2 cm. long is passed through, so that its end projects 0.5 cm. into the tube. The bottom is then flattened on an asbestos plate and annealed as usual. The anode, 7.5 cm. in length, is made from platinum wire 1 mm. in diameter coiled into a flat spiral 1.5 cm. in diameter. It is inserted in a chuck carried by the rotator, which is also provided with three pulleys varying from 2 to 5 cm. in diameter. These pulleys are connected by a belt to either of two pulleys on the motor. With this arrangement the rotation of the anode can be varied from 100 to 1800 revolutions per minute. During the experiment, an amperemeter, a voltmeter, and a rheostat allowing of resistance from 0.1—100 ohms are kept in the circuit. L. DE K.

Use of the Rotating Cathode for the Estimation of Cadmium taken as the Sulphate. CHARLES P. FLORA (*Amer. J. Sci.*, 1905, [iv], 20, 268—276).—Cadmium in solutions of the sulphate may, by the use of a rotating cathode, be estimated electrolytically when the solution contains excess of sulphuric acid, acetates, cyanides, pyrophosphates, phosphates, oxalates, urea, formates, or tartrates, and the conditions under which the best results were obtained are given in the paper (Abstr., 1904, ii, 770). L. M. J.

Electrolytic Estimation of Cadmium with the Use of a Rotating Anode. ALICE L. DAVISON (*J. Amer. Chem. Soc.*, 1905, 27, 1275—1287).—A lengthy paper, fully illustrated with curves and tables, on the electrolytic precipitation of cadmium in presence of the following electrolytes: sulphuric acid, ammonia and ammonium sul-

phate, sodium formate, ammonium formate, sodium acetate, ammonium acetate, potassium cyanide in presence of sodium hydroxide, ammonium succinate, sodium succinate. Ammonium lactate or sodium lactate cannot be recommended.

Processes are also given for the separation of cadmium from magnesium, iron, nickel, and cobalt. For working details, the original paper should be consulted.

L. DE K.

Rapid Electrolytic Estimation of Lead. RALPH O. SMITH (*J. Amer. Chem. Soc.*, 1905, 27, 1287—1293).—Twenty-five c.c. of lead nitrate solution containing not more than 0.25 gram of metal are mixed with 20 c.c. of nitric acid of sp. gr. 1.4 and diluted with water to 115 c.c. The solution is then subjected to electrolysis, using a rotating electrode (in this case the cathode) making about 450 revolutions per minute.

The following conditions are necessary to ensure success: temperature, 70°; time, at least 15 minutes; volts, 3.7—4.0; amperes, ND_{100} 11—13.

The lead separates as dioxide, which is first washed with water without interrupting the current, and then with alcohol and ether. It is dried for at least half an hour at 200—230°. In calculating the lead, the factor 0.8643 should be employed if the weight of the precipitate exceeds 0.1 gram.

L. DE K.

Volumetric Methods for Estimating Copper. GUSTAVE FERNEKES and ARTHUR A. KOCH (*J. Amer. Chem. Soc.*, 1905, 27, 1224—1240).—A criticism of the various volumetric processes for the estimation of copper, including the cyanide process and its modifications, the ferrocyanide method, the thiocyanate method, the acidimetric method, the permanganate method, and the iodometric method, which the authors consider to be the most suitable for ores.

The solution of the copper ore obtained in due course is treated with a strip of aluminium, the precipitated copper is washed, redissolved in nitric acid, and boiled. The solution is diluted, rendered alkaline with ammonia, again boiled, and then acidified with acetic acid. When cold, 3 grams of potassium iodide are added, and the liberated iodine is titrated with $N/10$ sodium thiosulphate.

L. DE K.

Electrolytic Estimation of Mercury [in Cinnabar] with the Use of a Rotating Anode. RALPH O. SMITH (*J. Amer. Chem. Soc.*, 1905, 27, 1270—1275).—About 0.5 gram of the ore is repeatedly boiled with solution of sodium sulphide of sp. gr. 1.06. About 60 c.c. in all will be required for complete extraction. The united filtrates are then subjected to electrolysis, using a rotating anode. The conditions essential to success are: time, not less than 20 minutes; volts, 6—5.1; amperes, ND_{100} 6. The results compare favourably with the usual combustion with lime. The process also applies to other mercury salts.

L. DE K.

Occurrence of Alumina in Plants. HENRI PELLET and CH. FRIBOURG (*Ann. Chim. anal.*, 1905, 10, 373—376).—The authors have

examined sugar-cane and beetroots for alumina, and find that the latter is present in the ashes of the plants in only very minute quantity. The method employed for the estimation of the alumina in the plant-ash was as follows: after separation of the silica, the hydrochloric acid solution was nearly neutralised with ammonia and oxidised by the addition of a few crystals of potassium chlorate. Two grams of ammonium phosphate and 10 grams of ammonium thiosulphate were then added and the mixture boiled for fifteen minutes, 15 grams of acetic acid being afterwards added. The precipitate of aluminium phosphate was collected on a filter, ignited, and weighed. W. P. S.

Detection of Nickel [in Presence of Cobalt]. STANLEY R. BENEDICT (*J. Amer. Chem. Soc.*, 1905, 27, 1360—1361).—The neutralised solution is saturated with potassium chloride and a little solid potassium nitrite, or 1 c.c. of its saturated solution, is added. The mixture is then acidified with acetic acid and shaken for half a minute. The cobalt is completely precipitated, and although some of the nickel is also deposited, sufficient remains in solution and may be precipitated with ammonium sulphide and then further identified by the bead test.

L. DE K.

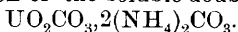
The Sodium Hydroxide Method of Estimating Molybdenum in Steel. GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1905, 27, 1240—1246).—A reply to Cruser and Miller (*Abstr.*, 1904, ii, 593), who state that iron also goes into solution to some extent, and that, therefore, the separation of molybdic acid from iron oxide by means of sodium hydroxide is untrustworthy.

The author states that the small quantity of iron found in their experiments has most likely passed through mechanically. When carried out in the following manner, the process gives technically accurate results.

0.8 gram of the steel is dissolved in nitric acid, evaporated to dryness, boiled with 25 c.c. of hydrochloric acid, and evaporated with 10 c.c. of dilute sulphuric acid (3:1) until fumes appear. Fifty c.c. of water are added, and the solution is poured gradually into 100 c.c. of the alkali hydroxide (454 grams sodium hydroxide + 2100 c.c. water). After diluting to 200 c.c., 100 c.c. of the filtrate are acidified with 15 c.c. of sulphuric acid, reduced with zinc, and titrated with permanganate.

L. DE K.

Properties of Ammonium Uranate. FEDERICO GIOLITTI (*Gazzetta*, 1905, 35, ii, 145—150. Compare *Abstr.*, 1904, ii, 783).—The principal errors in the estimation of uranium by precipitation as ammonium uranate from solutions of uranyl salts consist in (1) the formation of colloidal ammonium uranate, which may be prevented, not by large quantities of ammonia as Rose recommended, but by ammonium salts, especially the chloride; (2) a loss of uranium owing to the absorption of carbon dioxide from the air by ammonia solutions and subsequent formation of the soluble double salt,



The author consequently adopts the following method of working:

300 to 400 c.c. of solution containing 0.1—0.2 gram of uranium in the form of uranyl salt and about 1 gram of ammonium chloride are heated to boiling in a platinum or porcelain basin. The boiling is stopped, and the solution kept well stirred while ammonia solution (one part concentrated solution mixed with ten parts of water) is gradually added until the liquid smells distinctly of it. The precipitated ammonium uranate is washed by decantation several times with boiling 0.2—0.5 per cent. ammonium chloride solution, separated by filtration, and again washed with the same solution. It is then converted either into U_3O_8 by ignition in air or into UO_2 by ignition in a stream of hydrogen, the heating being gentle until the ammonium chloride has been expelled.

T. H. P.

Estimation of Titanic Acid in Soils and Ashes of Plants.

HENRI PELLET and C. FRIBOURG (*Chem. Centr.*, 1905, ii, 1193—1194; from *Bull. Assoc. Chim. Sucre Dist.*, 23, 67—71).—*Colorimetric Process.*—0.5 gram of finely-powdered dry soil or 2.5 grams of plant-ash are put into a platinum crucible containing 15 grams of pure hydrofluoric acid, 1 c.c. of sulphuric acid is added, and the whole is evaporated to dryness. The residue is then fused with 5 grams of potassium hydrogen sulphate, and the mass is dissolved in 15 per cent. sulphuric acid at a temperature not exceeding 60°. When cold, the liquid is made up to 100 c.c., and 10 c.c. are mixed with 5 c.c. of hydrogen peroxide. The colour generated is then compared as usual with that obtained by means of a known amount of titanium. If much titanium is present, the solution must be diluted suitably.

Gravimetric Methods.—If soils contain at least 2 per cent. of titanium dioxide, 3 grams of the sample are evaporated with 30 grams of hydrofluoric acid and 3 grams of sulphuric acid, and the residue is fused with 15 grams of potassium hydrogen sulphate. The mass is then heated at 60° with 200—250 c.c. of water, diluted to 300 c.c., and filtered. Forty c.c. of the filtrate are then titrated with aqueous potassium hydroxide, 10 c.c. of which represent 5 grams of potassium hydrogen sulphate. To 250 c.c. of the filtrate is then added so much alkali that there still remains 5 grams of free potassium hydrogen sulphate, the liquid is boiled for two hours with addition of dilute sulphurous acid of sp. gr. 1020—1025, added in three portions of 50 c.c. each. The precipitate is collected and ignited, and then fused with 2 grams of potassium carbonate; the mass is treated with boiling water, and the titanate formed washed with a 2 per cent. solution of potassium carbonate. A small portion, however, passes into solution and should be estimated separately. The titanate is now fused with 1 gram of potassium hydrogen sulphate and the titanic acid separated in the manner described.

When dealing with soils containing less than 1 per cent. of titanium dioxide, twice 5 grams of the ignited soil are fused with 10 grams of potassium carbonate and 10 grams of sodium carbonate; the mass is evaporated with hydrochloric acid, the silicic acid is expelled by evaporation with hydrofluoric and sulphuric acids, and to the residue is added the ignited precipitate formed by ammonia in the

hydrochloric acid solution. The whole is then fused with 15—20 grams of potassium hydrogen sulphate and treated as directed.

Of ashes which contain less than 0.2 per cent. of titanium dioxide, 50 grams are taken, and the silica separated therefrom is treated first with hydrofluoric and sulphuric acids, and the residue is then treated several times with potassium carbonate, potassium hydrogen sulphate, &c., as directed, until a pure titanium dioxide is obtained. To the filtrate from the silica are added 0.5 gram of sublimed ferric chloride and 25 grams of ammonium phosphate; the mixture is evaporated in a platinum dish and the residue ignited to expel ammonium salts. The mass is then digested in dilute hydrochloric acid and the residue submitted to fusion with potassium carbonate and finally with potassium hydrogen sulphate as described.

L. DE K.

Zirconium Oxychloride as a means of Testing for Zirconium. RUDOLF RUER (*Zeit. anorg. Chem.*, 1905, 46, 456—459).—The formation of zirconium oxychloride, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, is recommended as a means of detecting the presence of zirconium. The precipitate obtained from the experimental material by means of ammonia is separated from the filter-paper and dissolved in hydrochloric acid. The solution is evaporated to dryness on the water-bath and then dissolved in a little water. Concentrated hydrochloric acid is added drop by drop so as to obtain a precipitate of the oxychloride; this precipitate goes into solution on warming the liquid, and on cooling separates again in crystals which have a characteristic appearance (thin prisms) under the microscope.

Hauser's statements as to the properties of zirconium compounds (this vol., ii, 531) are criticised.

D. H. J.

Heating of Mineral Oils when shaken with Concentrated Sulphuric Acid. RICHARD KISSLING (*Chem. Zeit.*, 1905, 29, 1086).—Seventy-five c.c. of the sample are introduced through a side opening into a cylindrical vessel of special construction, and 25 c.c. of sulphuric acid are then very carefully allowed to run from a pipette to the elongated bottom of the instrument. The cylinder is conveniently furnished with taps at both ends, but these are not absolutely necessary. After inserting the thermometer and placing the instrument in a wooden casing, the thermometer is read after its indication has become constant, and the whole is then shaken until the temperature no longer rises but begins to fall.

A number of experiments with various mineral and lubricating mineral oils are recorded.

L. DE K.

Apparatus for determining the Melting Point of Asphalt. HUGO BAUER (*Chem. Rev. Fett-Harz-Ind.*, 1905, 12, 258—260).—A modification of the Kraemer-Sarnow apparatus is described. A test-tube, 4 cm. in diameter and about 15 cm. long, is hung in the neck of a flask so that its lower end is immersed in the water (or other liquid) placed in the flask. The test-tube is closed by a cork through which three holes have been bored; the centre hole is for the

thermometer and the other two for the testing cylinders. The latter consist of open tubes 7 mm. in diameter and 15 cm. long. A mark is placed on the tubes 5 mm. from the lower end, and a second mark above it at such a distance that the space between the marks will hold exactly 5 grams of mercury. Each tube is also provided with a closely-fitting piston attached to a rod reaching above the upper end of the tube. The tubes are filled as follows: the piston is pushed in until its lower end is at the upper mark on the tube: the tube is then inverted, mercury poured in to fill the space between the marks, and finally the melted asphalt. After cooling, the asphalt is trimmed with a knife level with the end of the tube and the latter inserted through the hole in the cork of the test-tube. The second tube may be filled with another sample or serve as a duplicate. The melting point is then determined as in the original method.

W. P. S.

Examination of *o*-Nitrotoluene for the Presence of Small Quantities of *p*-Nitrotoluene. ARNOLD F. HOLLEMAN and COENRAAD L. JUNGUS (*Chem. Centr.*, 1905, ii, 988—989; from *Chem. Weekblad*, 2, 553—554. Compare this vol., i, 272).—The presence of 0.4 per cent. of *p*-nitrotoluene in a sample of *o*-nitrotoluene which had been obtained by Meister, Lucius, & Brüning's method (this vol., i, 639) was inferred from the fact that the crystals from the mother liquor of the acetyl derivative of the toluidine prepared from the sample melted at a temperature one degree lower than that of the pure compound.

E. W. W.

Amount of Sodium Salts naturally occurring in Wine. OTTO KRUG (*Zeit. Nahr. Genussm.*, 1905, 10, 417—421).—From the results of the analyses of forty-eight samples of wine it is seen that the total amount of sodium oxide (Na_2O) varies from 0.0004 to 0.0060 per cent. Even where the vines had been partially manured with sodium nitrate (Chili saltpetre), the latter figure was not exceeded. In thirty-eight of the above-mentioned samples, the sodium oxide was not more than 1 per cent. of the total ash. There is but little difference between red and white wines in this respect. The author therefore concludes that any German wine containing more than 0.010 per cent. of sodium oxide has been artificially prepared.

W. P. S.

Detection of Asaprol [β -Naphtholsulphonate]; Estimation of Methyl Alcohol in Presence of Formaldehyde. HENRY LEFFMANN (*Chem. Zeit.*, 1905, 29, 1086).—A mercurial reagent is prepared by dissolving mercury in twice its weight of nitric acid and diluting the solution with five times its bulk of water. In order to detect the preservative asaprol [β -naphtholsulphonate] in milk, 10 c.c. of the sample are mixed with 0.5 c.c. of the reagent, which will cause a yellow coloration should asaprol be present. To detect the same in wine or fruit juices, 25 c.c. of the sample are acidified with sulphuric acid and shaken with an equal volume of ether, light petroleum, chloroform, or carbon tetrachloride; the author prefers light petroleum. The solution is then shaken with addition of a few drops of the reagent, and in

presence of asaprol the mercury solution soon turns yellow and then red. Benzoates and salicylates give no reaction.

Methyl (also ethyl) alcohol may be completely freed from formaldehyde by distilling the mixture with a slight excess of potassium cyanide. It is advisable to test a little of the mixture for possible traces of undecomposed formaldehyde by the phenylhydrazine-nitroprusside reaction. The distillate is now tested for methyl alcohol by the well-known red hot copper (formalin) test. L. DE K.

Estimation of Glycerol in Soap-lyes. H. STRAUSS (*Chem. Zeit.*, 1905, 29, 1099—1100).—From 10 to 30 grams of the sample are introduced into a 100 c.c. flask and a slight excess of basic lead acetate is added. In the presence of much salt it is as well to add first 1 gram of silver oxide suspended in water. The whole is diluted to 100 c.c. and 10 c.c. of the filtrate are used for the analysis; 5—6 grams of powdered potassium dichromate are put into a 250 c.c. distilling flask and the glycerol solution is introduced through a separating funnel, followed by 20 c.c. of water and then by 20 c.c. of dilute sulphuric acid (1:2). The flask is connected with a short reflux condenser in order to condense most of the steam. The whole is boiled for twenty minutes, whilst air, which has passed through a Drexel wash-bottle containing potassium hydroxide solution, is drawn through by means of an aspirator. The carbon dioxide formed by the oxidation of the glycerol is first passed through a series of five calcium chloride tubes and then absorbed in the usual weighed potash apparatus. After passing the current of air for another twenty minutes, the potash apparatus is reweighed. The increase in weight $\times 0.6976$ = glycerol in the 10 c.c. taken. L. DE K.

Spectroscopic and Colour Reactions of Important Sugars. ERW. PINOFF (*Ber.*, 1905, 38, 3308—3318. Compare this vol., ii, 289).—The following sugars have been investigated: arabinose, rhamnose, dextrose, mannose, galactose, lævulose, sorbose, sucrose, lactose, maltose, raffinose. All these, with the exception of arabinose, give the Molisch reaction when 0.05 gram is mixed with 10 c.c. of a sulphuric acid-alcohol mixture and 0.2 c.c. of a 5 per cent. alcoholic solution of α -naphthol. Considerable differences are noticed as regards length of time of heating required. When similar experiments are made with the addition of 10 c.c. of ethyl alcohol, only lævulose, sorbose, sucrose, and raffinose give the reaction, each yielding a single band at 5088 $\mu\mu$. With the more concentrated solution, each of these sugars gives two bands at 5736 and 5088, whereas the other sugars give a single band at 5325.

Similar experiments have been made with β -naphthol. With the more dilute solution, lævulose gives a reddish-brown, and sorbose a yellowish-green, coloration after twenty-five minutes at 95—98°; the remaining sugars give no reaction even after forty-five minutes. With the more concentrated solution, lævulose, sorbose, sucrose, and raffinose react after four minutes, yielding solutions with an absorption band at 5050 $\mu\mu$.

Experiments with resorcinol, using 5 c.c. of alcohol, 5 c.c. of the alcohol-acid mixture, and 0.2 c.c. of a 5 per cent. resorcinol solution,

show that all give a band at 4875 with the exception of arabinose, rhamnose, mannose, and galactose. The band is given most readily by lævulose, sorbose, sucrose, and raffinose.

All the sugars yield a yellow precipitate when heated for twenty minutes with 10 c.c. of a 10 per cent. ferric chloride solution. They also, with the exception of sucrose and raffinose, reduce potassium ferrocyanide and ferri cyanide and lead acetate. Only sorbose and lævulose yield precipitates when heated with equal quantities of 5 per cent. solutions of potassium dichromate and ammonium chloride; the precipitate is formed after twelve minutes with sorbose and after twenty with lævulose.

Lævulose yields a characteristic blue coloration when 0.1 gram is heated for three minutes with 10 c.c. water, 10 c.c. of 4 per cent. ammonium molybdate solution, and 0.2 c.c. of glacial acetic acid. Arabinose, rhamnose, galactose, mannose, and sorbose give a green coloration only after some thirty minutes. Mineral acids must not be present in testing for lævulose by this method, as most sugars in the presence of mineral acid give a blue coloration with ammonium molybdate.

J. J. S.

Diphenylhydrazine as a Reagent for Lactose. W. C. DE GRAAFF (*Chem. Centr.*, 1905, ii, 991; from *Pharm. Weekblad*, 42, 685—686).—When a drop of diphenylhydrazine and 2—3 drops of glacial acetic acid are boiled with a few mg. of lactose, the brownish-violet coloration which is first formed becomes successively yellow and brownish-red, and the viscosity of the solution increases. When the mixture is further heated, it becomes blackish-green and finally brown. If the green solution is treated with a few c.c. of 70 per cent. alcohol, a characteristic green liquid is obtained. The green dye is also soluble in amyl alcohol, chloroform, and ether, but insoluble in water or carbon disulphide. Arabinose, lævulose, dextrose, galactose, mannose, sucrose, maltose, melibiose, dextrin, amyllum, and gum arabic only form deep reddish-brown colorations with diphenylhydrazine. This reaction may be used to detect lactose in mixtures of equal parts of lactose, dextrose, and sucrose, and in mixtures of sucrose with 10 per cent. of lactose.

E. W. W.

Separation of Starch Coagulum and Amylocellulose. JULES WOLFF (*Ann. Chim. anal.*, 1905, 10, 389—392).—The principle of the method described is as follows: equal weights of the starch are placed in three flasks and converted into a paste by heating under pressure with water. After cooling, the contents of one of the flasks (*a*) receives the addition of 20.5 c.c. of a 10 per cent. malt infusion. The other two flasks (*b* and *c*) receive 0.5 c.c. of the same infusion. The flask *a* is kept at a temperature of 60°; the contents of flask *b* are allowed to coagulate at the ordinary temperature for three hours, 20 c.c. of the *boiled* malt infusion are then added and the volume made up to 200 c.c., whilst the contents of flask *c*, after being allowed to coagulate as in the case of flask *b*, are treated with 20 c.c. of the malt infusion (*not boiled*) and saccharified at a temperature of 70° before diluting to 200 c.c. At the end of three hours, the contents of flask *a* are also made up to 200 c.c. All three solutions are then filtered and

100 c.c. of each of the filtrates heated in an autoclave at a temperature of 120° for twenty minutes, and the reducing power of each estimated and calculated into starch. The difference between *a* and *b* gives the weight of the coagulum, and the difference between *a* and *c* that of the amylocellulose.

W. P. S.

Estimation of Formaldehyde. CARL GOLDSCHMIDT (*J. pr. Chem.*, 1905, [ii], 72, 343—344. Compare Abstr., 1903, i, 82).—A *résumé* of some methods which have been proposed for the estimation of formaldehyde (compare Legler, Abstr., 1883, 1035; 1889, 579; Trillat, Abstr., 1893, ii, 439; Grützner, Abstr., 1897, ii, 166; Romijn, *ibid.*).
G. Y.

Estimation of Certain Aldehydes and Ketones in Essential Oils. SAMUEL S. SADTLER (*J. Amer. Chem. Soc.*, 1905, 27, 1321—1327).—Further details of and experiments on the process already published (Abstr., 1904, ii, 372). Contrary to the statement of Burgess (Abstr., 1904, ii, 371), the author finds that carvone reacts not with one but with two mols. of sulphite, and that citronellol does not react.

L. DE K.

Toxicological Detection of Hydrocyanic Acid. DOMENICO GANASSINI (*Chem. Centr.*, 1905, ii, 1036—1037; from *Boll. Chim. Farm.*, 44, 519—525. Compare Abstr., 1904, ii, 758).—An account of the different distribution of hydrocyanic acid in the blood and organs of the body after it has been administered in various ways. The number of instances where it is not found indicates that it is completely changed in the animal body.

W. D. H.

Evaluation of Official Mercuric Cyanide. ERWIN RUPP (*Arch. Pharm.*, 1905, 243, 468—469).—One gram of the sample is dissolved in water and made up to 100 c.c.; 10 c.c. of the solution are mixed with a little water and 10—20 c.c. of approximately *N*-potassium hydroxide solution in a 200 c.c. stoppered flask; 25 c.c. of *N*/10 iodine solution are added with gentle agitation, and the mixture is allowed to remain for about two hours at the ordinary temperature, or for 20—30 minutes on the water-bath. The liquid is then diluted with water to about 100 c.c. and acidified with dilute hydrochloric acid, and the iodine liberated is titrated after 1—2 minutes with *N*/10 thiosulphate solution. In the case of a pure sample, 15.87 c.c. of *N*/10 iodine solution should be used up in oxidising the cyanide to cyanate; consequently the volume of *N*/10 thiosulphate solution required should be 9.3—9.1 c.c., corresponding with a purity of 99—100 per cent.

C. F. B.

Titrimetric Estimation and Separation of Cyanides, Thiocyanates, and Chlorides. ERWIN RUPP (*Arch. Pharm.*, 1905, 243, 458—467).—A known quantity of the cyanide dissolved in 10 c.c. of water is mixed with 10 c.c. of approximately *N*-potassium hydroxide solution in a stoppered bottle, 25 c.c. (representing a considerable excess) of *N*/10 iodine solution is added with gentle agitation, and the

whole is then allowed to remain for three hours at the ordinary temperature, or for thirty minutes on the water-bath, when the cyanide becomes oxidised to cyanate. Finally, the contents of the bottle are diluted to about 100 c.c. and acidified with dilute hydrochloric acid, and the iodine liberated is titrated with $N/10$ thiosulphate solution. Each 1 c.c. of $N/10$ iodine solution oxidises 0.0013 gram of cyanogen.

A known quantity of thiocyanate dissolved in 10 c.c. of water is mixed with 10—20 c.c. of approximately N -potassium hydroxide solution, 25 c.c. (a considerable excess) of $N/10$ iodine solution are added, and the whole is allowed to remain for four hours at the ordinary temperature or thirty minutes on the water-bath; it is then cooled, acidified with dilute hydrochloric acid, and titrated with $N/10$ thiosulphate solution. The thiocyanate is oxidised to sulphuric acid and cyanate, every 1 c.c. of $1/10$ iodine solution oxidising 0.000725 gram of thiocyanogen (CNS).

For the estimation of a mixture of cyanide and thiocyanate, a known quantity of the mixture is allowed to remain for four hours with excess of $N/10$ iodine solution and about 2 grams of sodium hydrogen carbonate; the cyanide is converted into cyanogen iodide and the thiocyanate into sulphuric acid and cyanogen iodide. The mixture is then acidified cautiously with hydrochloric acid, when iodine is regenerated from the cyanogen iodide, only that which has oxidised the sulphur of the thiocyanate to sulphuric acid remaining permanently as iodide. Finally, the iodine liberated is titrated with $N/10$ thiosulphate solution. Each 1 c.c. of $N/10$ iodine solution used corresponds with 0.000967 gram of CNS. The total amount of cyanide and thiocyanate together is estimated by oxidation in the presence of potassium hydroxide as described above.

In a mixture of cyanide, thiocyanate, and chloride, first the thiocyanate, and then the thiocyanate and cyanide together, are determined as just described; finally, all three are determined together by adding a known quantity of the mixture to excess of $N/10$ silver solution in a 100—200 c.c. graduated flask, diluting to the mark, filtering, mixing a measured volume of the filtrate with plenty of nitric acid and about 5 c.c. of iron alum solution (1 : 10), and titrating the excess of silver with $N/10$ thiocyanate solution.

In none of the experiments quoted did the experimental error quite reach 1 per cent. of the quantity estimated. C. F. B.

Lead Malate and Barium Citrate. T. C. N. BROEKSMIT (*Chem. Centr.*, 1905, ii, 886—887; from *Pharm. Weekblad*, 42, 637—640. Compare Abstr., 1904, ii, 688).—Citric acid and malic acid give the iodoform reaction. Pure malic acid is prepared by treating an aqueous solution of the acid with lead acetate and decomposing the lead malate with sulphuric acid. In order to detect citric acid in the presence of malic acid, the solution is treated with barium chloride and ammonia, and the insoluble barium citrate tested with potassium permanganate, ammonia, and iodine for the iodoform reaction.

E. W. W.

Detection of Pyrrolidine-2-carboxylic Acid. D. ALEXANDROFF (*Zeit. physiol. Chem.*, 1905, 46, 17—18).—This substance in either the active or racemic state may be detected by means of its picrate. The characters, solubilities, &c., of the two picrates are described; that from the racemic form melts at 135—137°; that from the active at 153—154°.

W. D. H.

Composition and Analysis of Milk. H. DROOP RICHMOND (*Analyst*, 1905, 30, 325—329).—The average composition of 15,910 samples of milk analysed during the year 1904 is given. The average amount of fat was 3.74 per cent., being a little less than that found in 1903 (*Abstr.*, 1904, ii, 522).

A number of experiments was carried out with a view to ascertaining the correct volume of the divisions of the necks of the bottles used in Gerber's method. Each division should have a volume of 0.126 c.c., and will then indicate 1 per cent. of fat. The exact diameter of the neck is of no importance. The volume of the fat obtained in the Gerber method is about 1.025 the volume of the fat in the milk. Neglect of the volume of the fat between the upper and the lower parts of the meniscus is partly compensated by the decrease in weight of the milk delivered by an 11 c.c. pipette with increasing quantities of fat.

The results of a sample of human milk are given: total solids, 10.39 per cent.; fat, 1.98 per cent.; sugars, 6.40 per cent.; proteids, 1.75 per cent.; ash, 0.26 per cent. The amount of fat in this sample is much below the average.

W. P. S.

Occurrence in Milk Serum of Substances which react with Naphthalene- β -sulphonic Chloride. ROBERT STRITTER (*Milchw. Zentr.*, 1905, 1, 444—447).—Milk serum obtained by precipitating the proteids of fresh milk with an acid alcoholic solution of tannin, removing the excess of tannin with lead acetate and the latter with hydrogen sulphide, gave a residue on evaporation which contained no substances soluble in alcohol-ether. The absence of hippuric acid in normal fresh milk was thus proved. The serum was then rendered alkaline and shaken for many hours with an ethereal solution of naphthalene- β -sulphonic chloride. After separating the ether, the aqueous portion was acidified with hydrochloric acid and extracted with ether, ammonium sulphate being also added to "salt out" the amino-acid compounds. In no case could the presence of an amino-compound or other substance reacting with the naphthalene- β -sulphonic chloride be detected in normal fresh milk. An extremely minute quantity, however, of a nitrogenous substance was obtained, the identity of which was not established.

W. P. S.

Estimation of Fat and Water in Butter by Gerber's Method. A. HESSE (*Milchw. Zentr.*, 1905, 1, 433—444).—The two pieces of apparatus constructed by Gerber, one for the estimation of water in butter and the other for the combined estimation of water and fat in the same article of food, are both shown to give untrustworthy results. The latter neither agree between themselves nor with the quantities

found by the ordinary gravimetric method. The author therefore concludes that both pieces of apparatus are useless for estimating water and fat in butter.
W. P. S.

Testing Lard and Butter. EDUARD POLENSKE (*Chem. Centr.*, 1905, ii, 1130—1132; from *Arbb. Kais. Ges. A.*, 22, 557—575).—A criticism of the various methods in use for the testing of lard. Halphen's sulphur test, although extremely delicate, should not be taken without confirmation as a proof of the presence of cotton-seed oil, as the active principle of this oil which causes the reaction passes into the lard when the pigs are fed on cotton-seed cake. In such case, the phytosterol or the phytosterol acetate test should be applied. All adulterated lards yield an acetate-mixture the melting point of which exceeds 117°.

The phytosterol acetate test may also be successfully applied for ascertaining the purity of butter. As little as 7.5 per cent. of margarine or vegetable fats may be identified.
L. DE K.

Lard Testing. EDUARD POLENSKE (*Chem. Centr.*, 1905, ii, 1132; from *Arbb. Kais. Ges. A.*, 22, 576—583).—To detect small quantities of paraffin in lard, the unsaponifiable matter obtained from 100 grams of the sample is heated with 5 c.c. of sulphuric acid in a cylinder glass placed in a glycerol-water bath at 104—105° for an hour. When cold, the residue is shaken three times with 10 c.c. of light petroleum of low boiling point, the solution is repeatedly washed with water (to the second washing a little barium chloride is added) and then filtered and evaporated in a tared dish. Pure lard free from paraffin will yield about 0.003 gram of resinous residue.

When the unsaponifiable matter, or crude cholesterol, is intended for the phytosterol acetate test, it must be first freed from any paraffin by washing with light petroleum. This also removes undesirable resinous matters and leaves a residue richer in phytosterol.

L. DE K.

Detection of Coconut Oil in Lard. L. HORON (*Chem. Centr.*, 1905, ii, 1195; from *Rev. intern. falsific.*, 18, 85—86).—Five grams of the sample are heated with 10 c.c. of acetic acid of sp. gr. 1.055 at 60° and well shaken. When cooled to 40°, the bottom layer is transferred to a flat dish. The operation is repeated and the bottom layer is collected in a second and the top layer in a third dish. After driving off the acetic acid by heating for 30—40 minutes at 70—80°, the three portions are examined in the Abbé-Zeiss refractometer at 40°. In the case of pure lard, the three fractions will show a decreasing refraction, such as 50.5—49.7—49.3°, whilst with pure coconut oil an increasing refraction is obtained, 34.2—35—35.6°. In a mixture containing 15 per cent. of the latter, the refraction of the first shaking is lower than that of the residue 46.0—46.6—48.3°, therefore the reverse of what is noticed with pure lard.
L. DE K.

Estimation of Cyanamide and its Applications. RENATO PEROTTI (*Gazzetta*, 1905, 35, ii, 228—232. Compare this vol., ii, 196, 278).—The method given for the estimation of cyanamide is

based on the reaction occurring with silver nitrate in presence of ammonia, by means of which insoluble silver cyanamide is precipitated according to the equation: $\text{CN}\cdot\text{NH}_2 + 2\text{AgNO}_3 = \text{Ag}_2\text{CN}_2 + 2\text{HNO}_3$. The cyanamide solution is run from a burette into a definite volume of $N/100$ silver nitrate solution, rendered distinctly but not excessively ammoniacal, an excess of silver nitrate being left in the liquid. The precipitate is coagulated by gentle heating and removed by filtration, the silver in the filtrate being then estimated by titration with $N/100$ ammonium thiocyanate.

This method may be applied to the estimation of the calcium cyanamide in the artificial manure known as "kalkstickstoff," 1 c.c. of centinormal silver nitrate solution corresponding with 0.0004 gram of calcium cyanamide.

T. H. P.

Estimation of Acetanilide. WILLIAM A. PUCKNER (*Pharm. Rev.*, 1905, 23, 302—304).—Acetanilide and caffeine may be estimated in headache remedies by shaking out an acidified solution with chloroform, evaporating the latter, and weighing the residue, the caffeine being subsequently precipitated as the periodide. A number of experiments are described in which it was found that acetanilide may be volatilised during the evaporation of the chloroform solution unless special precautions are taken. Acetanilide is volatile at a comparatively low temperature. If the solvent be distilled from a flask and the residue dried below 60° , the loss is slight, and a constant weight is obtained after twenty-four hours. The residue obtained from an ether or chloroform solution of acetanilide is not pure acetanilide, but fairly trustworthy results may be obtained if, after the solvent has been distilled off, the flask is rotated until crystallisation sets in and the residue then dried at 95° for two hours. W. P. S.

Volumetric Estimation of Pyramidone and Antipyrine in the Presence of each other. GASTON PÉGUIER (*Ann. Chim. anal.*, 1905, 10, 392—393).—The picric acid method for the estimation of pyramidone alone (*Abstr.*, 1905, ii, 778) must be slightly modified if antipyrine is also present. The two substances are first precipitated together, as previously described, and the percentage weight of the precipitate obtained. This weight may be termed P . A second quantity of 0.231 gram of the sample is then dissolved in 10 c.c. of water, and the alkalinity of the pyramidone exactly neutralised with $N/10$ sulphuric acid, using helianthin as indicator. Forty grams of $N/20$ picric acid solution are now added, and the solution is titrated with $N/10$ potassium hydroxide solution after the addition of a little phenolphthalein. A second value is thus obtained, P' . Then $P - P'$ is the percentage of pyramidone in the sample, and by subtracting the value P from the pyramidone the percentage of antipyrine is obtained.

W. P. S.

Alkaloid Reactions. Veratrine (puriss. German Pharmacopœia IV). C. REICHARD (*Chem. Centr.*, 1905, ii, 857—858; from *Pharm. Centr.*, *H.*, 46, 644—649. Compare *Abstr.*, 1904, ii, 847; this vol., ii, 68, 127, 561, and 563).—When a small quantity of veratrine is

added to a crystal of potassium ferricyanide and water, the mixture evaporated, and the residue treated with a drop of a 25 per cent. solution of hydrochloric acid, a green coloration is formed, but if potassium ferrocyanide is used instead of potassium ferricyanide a snow-white mass is obtained. Other more or less characteristic tests with ammonium molybdate, ammonium metavanadate, mercurous nitrate, sodium iodate, potassium dichromate, tungstic acid, bismuth chloride, copper sulphate, copper oxychloride, formaldehyde, antimony chloride, and ferric chloride are also given in the abstract. E. W. W.

Estimation of Caffeine. WILLIAM A. PUCKNER (*Pharm. Rev.*, 1905, 23, 305—309).—When recovering caffeine from a chloroform solution, equally correct results are obtained by evaporating the chloroform from a shallow dish at a temperature of 50—60° and drying the residue at the same temperature for a further twenty-four hours, or by distilling off the solvent and drying the residue at 95—100° for about two hours. If the chloroform is distilled slowly and in such a way that active ebullition does not occur, decrepitation of the residue will not take place. W. P. S.

Use of Titanium Trichloride in Volumetric Analysis. II. EDMUND KNECHT and EVA HIBBERT (*Ber.*, 1905, 38, 3318—3326. Compare Abstr., 1903, ii, 509).—Coloured substances which yield colourless leuco-compounds may be readily titrated by means of a solution of titanium trichloride, the dye itself acting as indicator. All operations must be conducted in an atmosphere of carbon dioxide or other non-oxidising gas. Good results have been obtained with indigotindisulphonic acid in presence of Rochelle salt. With indigos of low grade, it is necessary first to remove impurities by Grossmann's method. Eosin A and Rhodamine B yield good results in the presence of Rochelle salt and alcohol. Pararosaniline hydrochloride, pararosanilinetrisulphonic acid, malachite-green, crystal-violet, tolusafranine, indoin, and methylene-blue have also been analysed. Hydrogen peroxide may be estimated volumetrically by means of titanium trichloride, the disappearance of the yellow colour being taken as the end-point. Ammonium persulphate solutions may be estimated by adding an excess of titanium trichloride and titrating this excess with ferric salts.

Tin may be estimated by solution in hydrochloric acid, addition of an excess of ferric salt, and titration of the excess with titanium trichloride. J. J. S.

Estimation of Urinary Indican by Meisling's Colorimeter. H. P. T. OERUM (*Zeit. physiol. Chem.*, 1905, 45, 459—465. Compare Abstr., 1904, ii, 449).—Bouma's isatin method is used, namely, condensation of indoxyl and isatin to indigo-red, and colorimetric estimation in chloroform solution. The method gives good results.

W. D. H.